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HIGH EFFICIENCY GENERATION OF HYDROGEN FUELS USING SOLAR THERMAL-CHEMICAL SPLITTING OF WATER (SOLAR THERMO-CHEMICAL SPLITTING FOR H₂)

ANNUAL REPORT FOR THE PERIOD
OCTOBER 1, 2003 THROUGH SEPTEMBER 30, 2004

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DECEMBER 2010

GENERAL ATOMICS

DISCLAIMER

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GENERAL ATOMICS

1. INTRODUCTION

This work investigates the possibility of economic thermochemical production of hydrogen from water, using concentrated solar energy as the heat source. The first effort, the subject of this year's work, was to investigate all possible thermochemical cycles to determine which cycles might be well suited to use with concentrating solar energy devices. The effort was then to (1) find and organize information on known thermochemical water-splitting cycles, (2) define the important characteristics of the solar devices which would affect cycle selection, (3) define quantifiable criteria that could be easily used to screen the cycles for use with each solar device, eliminating unsuitable cycles, and (4) performing a semi-rigorous evaluation of the cycles that passed the initial screening, to find those cycles that required the least thermal energy to produce hydrogen. The first three items together make-up our Phase 1 screening task and the fourth item is our Phase 2 screening task.

2. PHASE 1 SCREENING

The goal of Phase 1 screening was to list all thermochemical cycles and then, on the basis of pertinent criteria and quantitative metrics, to rank the potential that a cycle could be economically implemented, and to remove from further consideration those cycles having low potential for ultimate success. As the criteria varied with the type of solar device, the scoring had to be repeated for each solar device.

Objective measures were found to assign a criteria score for each cycle, and then points (0–10 pts) were assigned to the range of scores. For instance, on criteria 2 (number of difficult separations), a given cycle would have a score of 4 separations, and 4 separations would be assigned 2 points. Thus, each cycle would be assigned 0–10 points, on each of 16 criteria. Each criterion was then weighted (so as to be more or less important), to yield a total score. The weighting of criteria was usually "the same" across the 4 different solar devices, but on criterion 8, each device had a separate weighting. This total score was then normalized so that the final score corresponds to the percent of maximum possible points.

2.1. The Phase 1 Criteria

The following 16 criteria were constructed as quick and simple measures of potentially viable thermochemical criteria (Table 1). Each criteria is worth 0-10 points.

Criteria 1-6. Economic Considerations

Criterion 1. The number of steps or fundamental reaction equations in the cycle.

A two step cycle would seem to be less complex than a 5 step cycle: fewer movements of material, fewer separations, fewer chemicals-all other things being equal.

No.	Criteria	CRITERIA SCORE											Weighting Factor			
		0	1	2	3	4	5	6	7	8	9	10	Trough	Low Temp Tower	High Temp Tower	Dish
1	Number of chemical reactions	>4			4				3			2	6	6	6	10
2	Number of separation step	>4	4		3		2		1			0	4	4	4	8
3	Number of chemical elements	>4	4			3			2			1	0	0	0	0
4	Abundance of chemical elements	Ir	Rh, Te, Os, Ru, Re, Au	Pt, Bi, Pd, Hg, Se	Ag, In, Cd, Sb, Tm, Tl, Lu	I, Tb, W, Ho, U, Ta, Mo, Eu, Cs, Yb, Er, Hf, Sn, Ge	Th, As, Gd, Dy, Sm, Pb, Pr	Nb, Be, Nd, La, Ga, Y, Ce, Co, Sc, Rb	Cu, Zn, Zr, Ni, B, Ba, Li, Br, Cr, V, Sr	Mn, F, P	S, Ti, C, K, N	Ca, Mg, Cl, Na, Al, Fe, Si	3	3	3	3
5	Corrosiveness of chemicals	Oxidizing and complexing acid system [HI/I2, HCl/HNO3]	Hydrogen halides [HCl, HBr, HI]	Anhydrides of strong acids [SO3, N2O4] Strong Acids [H2SO4, HNO3]	Halogens [Cl2, Br2, I2]	Alkali oxides and hydroxides [NAOH, Li2O]	Alkaline oxides and hyddroxides [Mg(OH)2, CaO] Weak acids [H2S] Weak acid anhydrides [SO2] Transition metal salts [CuCl2]	Alkaline salts [MgSO4]	Alkali salts [NaCl, KBr, Li] Metal vapors [Zn, Sn]	Metal oxides and hydroixides [Fe(OH)3, FeO]	Non-metal oxides [As2O3] Metal specific corrosive gases [CO, NH3]	Non-corrosive gases [CO2, CH4]	7	7	7	7
6	Degree of solids flow	Batch flow of solids			Continuous flow of solid			Batch flow of gases/liquids through packed bed				Continuous flow of liquids and gases	10	7	7	10
7	Use of radiant heat transfer to solids	No high temp heating	Solid heated above 900°C	Solid heated above 1000°C	Solid heated above 1100°C	Solid heated above 1200°C	Solid heated above 1300°C	Solid heated above 1400°C	Solid heated above 1500°C	Solid heated above 1600°C	Solid heated above 1700°C	Solid heated above 1800°C	0	0	8	4
8a	Temperature of high temperature endothermic step	Less than 200°C or Greater than 650°C	200-210 °C or 625-650 °C	210-245 °C or 600-625 °C	245-260 °C or 625-600 °C	260-275 °C or 575-600 °C	275-290 °C or 550-575 °C	290-305 °C or 525-550 °C	305-320 °C or 500-525 °C	320-335 °C or 425-500 °C	335-350 °C or 400-425 °C	350-400 °C	10	0	0	0
8b	Temperature of high temperature endothermic step	Less than 500 °C or Greater than 2200 °C	500-550 °C or 2050-2200 °C	600-650 °C or 1950-2050 °C	650-700 °C or 1850-1950 °C	700-750 °C or 1750-1850 °C	750-800 °C or 1650-1750 °C	800-850 °C or 1550-1650 °C	850-900 °C or 1450-1550 °C	900-950 °C or 1350-1450 °C	950-1000 °C or 1250-1350 °C	1000-1250 °C	0	0	0	10
8c	Temperature of high temperature endothermic step	Less than 400 °C or Greater than 700 °C	400-410 °C or 685-700 °C	410-420 °C or 670-685 °C	420-430 °C or 655-670 °C	430-440 °C or 640-655 °C	440-450 °C or 625-640 °C	450-460 °C or 610-625 °C	460-470 °C or 590-610 °C	470-485 °C or 570-590 °C	485-500 °C or 550-570 °C	500-550 °C	0	10	0	0
8d	Temperature of high temperature endothermic step	Less than 500 °C or Greater than 2000 °C	500-530 °C or 1890-2000 °C	530-555 °C or 1780-1890 °C	555-585 °C or 1665-1780 °C	585-610 °C or 1555-1665 °C	610-640 °C or 1445-1555 °C	640-665 °C or 1335-1445 °C	655-695 °C or 1220-1335 °C	695-720 °C or 1110-1220 °C	720-750 °C or 1000-1110 °C	750-1000 °C	0	0	10	0
9	Compatible with thermal transients and/or diurnal storage*											O₂ release from high temp. oxide	0	0	5	5
10	Number of Papers	1	2-3	4-6	7-10	11-15	16-21	22-28	29-36	37-45	45-55	55 +	2	2	2	2
11	Scale of test	No lab. work			Test tube				Bench scale			Pilot scale	2	2	2	2
12	Efficiency and/or cost figures	No calculated efficiency			Calculated efficiency based on elementary reactions		Estimated efficiency with rough flowsheet		Calculated efficiency with detailed flowsheet			Detailed calculated cost	2	2	2	2
13	Chemical toxicity to human	IDEL >= 1 ppm U, Hg, As		0.001 < IDEL <= 0.01 ppm Ag, Pb, U (sol), Hg, Ni	0.01 < IDEL <= 0.1 ppm Co, U, V, Sb, Br₂, I₂	0.1 < IDEL <= 1 ppm Cr, H₂SO₄, Cu, Mn, Sn, Cl₂, KOH, NaOH	1 < IDEL <= 10 ppm FeOₓ, SO₂, HBr, Mo, HCl, C, H₂S	10 < IDEL <= 100 ppm NO₂, NH₃, CO	100 < IDEL <= 1000 ppm FeOx, NH₃, Mo cmpds, H₃PO₄, Mn Cmpds, C	1000 < IDEL <= 10,000 ppm C, CO, Mo	10,000 ppm< IDEL <= 100,000 ppm CO₂	Not a personnel hazard (N₂)	3	3	3	3
14	Long term toxicity to human	REL >=0.001ppm As, Be, Cd		0.001 < IDEL <= 0.01 ppm Ag, Pb, U (sol), Hg, Ni	0.01 < IDEL <= 0.1 ppm Co, U, V, Sb, Br₂, I₂	0.1 < IDEL <= 1 ppm Cr, H₂SO₄, Cu, Mn, Sn, Cl₂, KOH, NaOH	1 < IDEL <= 10 ppm FeOₓ, SO₂, HBr, Mo, HCl, C, H₂S	10 < IDEL <= 100 ppm NO₂, NH₃, CO	100 < IDEL <= 1000 ppm FeOx, NH₃, Mo cmpds, H₃PO₄, Mn Cmpds, C	1000 < IDEL <= 10,000 ppm C, CO, Mo	10,000 ppm< IDEL <= 100,000 ppm CO₂	Not a personnel hazard (N₂)	0	0	0	0
15	Environmental chemical toxicity	Category X (1 lb. reportable)		Category A (10 lb. reportable)		Category B (100 lb. reportable)		Category C (1000 lb. reportable)		Category D (5000 lb. reportable)			3	3	3	3
16	Reactivity with air and water	>6	6	5	4	3		2		1		0	2	2	2	2

Criterion 2. Number of difficult separations.

A very abbreviated flow diagram was constructed and used to determine the number of "difficult" separations needed, based solely on the fundamental equations of the cycles, for a viable process. The following types of separations were deemed difficult:

*   solid-solid separations, where the products are two solids

*   solid-liquid separations, where a filtration or other means would be needed

*   liquid-liquid separations, where two liquids (miscible or immiscible) were found.

*   gas-gas separations, such as separating O_2 from HCl.

*   Aqueous/non-aqueous, such as dehydrating aqueous H_2SO_4 to make anhydrous H_2SO_4

Gas-liquid and gas-solid separations were deemed "easy" and not counted.

Two other assumptions were made in this evaluation. First, the details of the separation were not evaluated. We looked solely at the fundamental separations to be made, not how we would do such. However, those evaluating the cycles had some discretion to say "if I cool the products by 100°C, I then change a difficult gas-gas separation into an easy gas-liquid separation, thereby improving the process and removing one gas-gas separation from the count." Second, since many steps are at equilibrium and do not proceed to completion, there would be recycle of all liquid and gas reactants from the product stream. We presumed solid reactants went to products completely. A significant fraction of the difficult separations resulted from recycle of gas or liquid reactants.

Criterion 3. Number of elements

The more elements present is a measure of the number of species to be dealt with. The greater the number of chemicals used indicates a more complex process.

Criterion 4. Abundance of chemicals

One would want to use very common chemicals and elements-they would be less expensive and readily available in large quantities. So this criterion looks at the abundance of the scarcest element in the cycle, and assigns points based on that limiting abundance.

Criterion 5. Use of non-corrosive chemicals

Corrosive chemicals lead to the use of more expensive non-corroding equipment. Chemical classes were constructed, for most to least corrosive, based on the expected corrosion of common metallic materials of construction.

Criterion 6. The extent that solid movement is required and the degree of batch processing.

The movement of solids in a process is difficult and costly. Movement of liquids and gases is "easy". Cycles having only continuous flow are easy and batch process are difficult. A cycle difficulty was ranked in the following order (1) continuous flow of gases and liquid, (2) batch flow of gasses and liquid through fixed beds of solids, (3) continuous flow of solids, and

(4) batch flow of solids. A cycle having multiple difficulties was ranked based on its least desirable characteristic

Criteria 7–9. Solar Considerations

Criterion 7. Radiant heat transfer

The transfer of heat to solids is favored at high temperatures, so cycles which use very high temperature solids have an advantage in this regard. This criterion set a sliding scale from below 900°C to above 1800°C.

Criterion 8. Temperature match to solar device

The highest temperature of a cycle, was compared to an optimum temperature range for a given solar device (mentioned above). If this temperature was near the "sweet spot", then a high point score was given to the cycle for this device. The further the temperature was from the "sweet spot", the lower the score.

For the purpose of rating cycles, cycles which were not well matched to a solar device, and received 0 points on this particular criterion, were excluded from further assessment even though they had high scores from the other criteria.

Criterion 9. Thermal transients and/or diurnal storage

This criterion is solar specific. Solar sources alone, work for only about 8–10 hours per day. The high temperature solar sources, considered here, use light concentrated by mirrors and thus cease to work when a cloud passes between the sun and the mirror field. So this criterion sought to answer "can the high temperature step STOP, safely, and then start up easily, when the sun stops and starts shining?" We found it very difficult to quantify this desirable characteristic of a cycle and, in the end, this requirement was reduced to "does the high temperature reaction evolve O_2 as the ONLY gas?" A cycle with this characteristic is compatible with direct solar energy input to solids in a windowless receiver. If yes, then the cycle receives 10 points; if not, the cycle receives 0 points.

Criteria 10–12. Literature and Level of Previous Effort

Criterion 10. Number of literature papers

If a cycle has been studied by many people, it is a measure of its attractiveness and viability. So the number of papers published, is an indication the cycle would more likely be viable, that problems would have been addressed, and a measure of more funding to support the work.

Criterion 11. Scale of test

A given cycle can be studied in labs with paper calculations, or confirmed in small scale apparatus. Has the cycle attracted enough work or support, to fund larger scale efforts: bench scale, pilot plant, etc. Cycles which have moved to larger scale, would appear to be "better" or more commercially likely to succeed.

Criterion 12. Energy efficiency and Cost

This criterion sought literature where the energy efficiency or cost has been evaluated from a flow sheet analysis. Cycles that have had such studies are more viable candidates than those which have not been studied.

Criteria 13–16. Environmental and Safety Studies

Criterion 13. Acute toxicity to humans

Ideally, every chemical used in a process is inherently and absolutely safe for human exposure. Practically, chemicals used in a plant would not be an immediate hazard for injury and death. This criterion looked at "the most dangerous chemical" in a cycle, as determined for acute human exposure. Points were assigned to the IDLH (Immediate Dangerous to Life and Health) values found in the NIOSH (National Institute of Occupational Safety and Health) Pocket Guide to Chemical Hazards.

Criterion 14. Long term toxicity to humans

A chemical can be safe for short term human exposure, but can be dangerous over long term low level exposure. This criterion looked at "the most dangerous chemical" in a cycle, as determined for chronic long term human exposure. Points were assigned to the REL (Recommended Exposure Limits) values taken from the NIOSH Pocket Guide to Chemical Hazards.

Criterion 15. Environmental toxicity

A chemical may be safe for human exposure, but damaging to the environment. This criterion looked at "the most dangerous chemical" in a cycle, as determined for environmental exposure, from EPA categories of reportable quantities discharged to the environment. These values were found in 40 CFR1, table 302.4 and Appendix A of part 355, and points were assigned.

Criterion 16. Reactivity with air or water

A chemical may be very useful in an enclosed setting, but in an accident exposed to air or water and become very hazardous. This criterion took the sum of the NFPA (National Fire Protection Association) hazard ratings for flammability and reactivity with air & water, for each chemical in a cycle, and assigned points based on the highest sum.

GA and UNLV performed most of the analysis to evaluate the cycles according to the criteria above. Some of the criteria required little evaluation (Criteria 1,3,4). UNLV did the literature survey and analysis on criteria 10–12. GA expended significant effort to provide input to the evaluation of the remaining criteria.

The weighting factors applied to each criterion were generated using the Six-Sigma methodology. Team members from GA, SNL, UNLV and CU determined that Capital Cost, Operating and Maintenance Costs, Development Risk, Applicability to the Diurnal Cycle and Environmental Risks were the important factors in cycle selection. Each of these factors was assigned an importance numerically and each of the criterion was assigned a relevance value of 0, 1, 3 or 9 with respect to its importance to the factor, as shown in Fig. 1. The product of the importance and relevance gave a guide to selection of weighting factors for each criterion, also shown in the figure.

	Importance	Few chemical Rxns	Few sep steps	Few Elements	Abbundant elements	Minimize corrosive chemicals	Minimize flow of solids	Use radient hx to solids	Temp Compatible with solar source	Oxygen release from high temp step	Many papers	Extensive testing	Basis for ecconomic justification	NIOSH IDL	NIOSH REL/TWA	EPA Release/reportability limit	Not flamabale/water reactive
Capital Cost	5	9	9	3	9	9	3	0	9	9	0	0	0	9	3	3	3
O&M	4	3	3	1	1	3	9	0	0	3	0	1	0	9	3	3	1
Development Risk	2	3	3	3	0	9	3	0	3	1	9	9	9	9	3	3	1
Diurnal Cycle	5	0	0	0	0	0	0	9	0	9	0	0	0	0	0	0	0
Environmental Risk	2	0	0	0	0	3	0	0	0	1	1	0	0	0	0	9	1
		63	63	25	49	81	57	45	51	106	20	22	18	99	33	51	23
Trough		6	4	0*	3	7	10	0	10	0	2	2	2	3	0*	3	0*
It tower		6	4	0*	3	7	7	0	10	0	2	2	2	3	0*	3	0*
Ht Tower		6	4	0*	3	7	7	8	10	5	2	2	2	3	0*	3	0*
Dish		10	8	0*	3	7	10	4	10	5	2	2	2	3	0*	3	0*

Fig. 1. Six-Sigma Quality Functional Diagram used in weighting factor analysis.

2.2. Sources of Cycles

The analysis required a literature search for how many thermochemical cycles were known. The initial input to this project was the roughly 115 cycles evaluated in the NERI project (2001) [1]. These cycles were located during a literature search performed at that time. Many of the cycles were described in review articles that gave only the basic chemical reactions and process temperatures, and lacked any reference to original data. A second source of cycles, was an expanded version of the original database compiled by the Claude Royer of Centre du Four Solaire Félix, Trombe d'Odeillo, France. Dr. Royer started with the NERI database and added additional cycles from his own literature collection. This work added some 50 cycles, for which there was very little overlap with the previous 115 cycles. Unfortunately, the literature references were not included with these cycles. The literature survey of this project, performed by UNLV, resulted in the addition of an additional 20 cycles. Finally, a few more cycles were added during the later stages of this work as they were encountered in the literature or suggested by individuals.

The literature search found published literature papers, conference proceedings, patents, and even a couple cycles found on the internet. We found cycles dating to the 1960's, and to literature from Japan, China, France & Germany, as well as the U.S. The search results come mostly from compiled databases (NERI and French), which may list a publication reference and an abstract, but we often did not have the actual paper. We sought papers only where there was more interest in a cycle, or when there was a need for more information than the abstract supplied. As one example, the abstract may not state a temperature for a reaction nor the phases, so we would not know if a given reaction was an electrolysis in an aqueous phase, or whether the

reaction was done in an aqueous solution, or whether the reaction occurred in the molten state. For cycles with such limited information, we sought the original literature. Given the distribution of sources, and many cycles were not in refereed sources, one can anticipate some cycles are not viable under scrutiny.

Upon identification, each cycle was assigned a unique process identification number (PID). Once all the cycles were assembled, we sought to eliminate duplicate cycles. Gaps in the PID numbers reflect cycles which have been merged with others. Duplicates are often not obvious, for a variety of reasons. As one simple example, one cycle may have 4 steps, one of which is

$$H_2SO_4 = H_2O + SO_2 + 1/2\ O_2$$
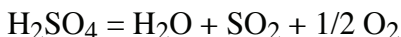
A similar cycle may have this single step written as 2 reactions, and thus 5 total steps

$$H_2SO_4 = H_2O + SO_3$$

$$SO_3 = SO_2 + 1/2\ O_2$$
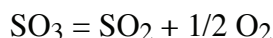
So the latter cycle is a five step process, while the former cycle is a four step cycle. We deemed these two cycles would be duplicates, and merged both cycles into one cycle.

Merging duplicates can have unintended consequences. The same cycle may have the same high temperature reaction, but the high temperature is different among the several merged cycles. Yet the maximum temperature sets the Criteria 8 scoring, and determines which solar device may be best for the cycle. In general in merging cycles, we looked at the scoring variations to see what the appropriate score and temperature would be. No simple and consistent method of assigning a merged score to one cycle became apparent. We used our best "judgment". The variation in scores tended to be small, and did not move a cycle from "winner" category to "loser" (or vis-a-versa) category.

Our compiled database thus resulted in a final total of 182 distinct cycles (Appendix 1).

2.3. The Four Types of Solar Devices

Four types of solar devices can concentrate the solar flux into a source of process heat. Each device has a practical range and size constraint.

Trough. The sun's light is focused by a mirrored parabolic through onto a heat transfer fluid or chemicals flowing through a pipe at the focus of the trough.

Tower. The sun's light is focused from sun-tracking mirrors (heliostats) to a small region atop a tower, where the heat transfer fluid (typically molten salt) is heated. The optimum temperatures were deemed in the 500–550°C. region.

Dish. The sun's light is focused on a receiver located at the focus of an axisymmetric parabolic heliostat. The optimum temperature range was considered to be 1000–1250°C.

Advanced Tower. The sun's light is focused, at a high concentration ratio, into a cavity receiver located atop a tower. The optimum temperature range was taken to be 750–1000°C.

Thus, each cycle had to be evaluated for its compatibility with each of the 4 devices. For instance, a cycle with a maximum temperature of 600°C would be very compatible with the tower. A cycle with a maximum temperature of 1200°C would not work well with a trough, but would work well with a dish or possibly an advanced tower. Criterion 8 is used to distinguish cycle compatibility with each of the solar devices.

2.4. Caveats, assumptions, warnings implicit in Phase 1 Screening

In assembling and screening the cycles in Phase 1, our methodology contains several caveats which need to be made explicit.

The temperatures assigned to the individual cycle reactions are not precise, for a variety of reasons. We usually assigned the temperature be what the cycle author presented. But we assigned a temperature under a variety of circumstances. First, sometimes the cycle information we had was not a complete journal article. We may have had a less complete document, maybe only an abstract, and thus temperature information may have been lacking. In these cases, we performed a calculation of ΔG for the reaction, as a function of temperature, and took the temperature where $\Delta G < 0$. For instance, if the calculation showed $\Delta G=0$ at 1123 C, we would assign 1150°C, where ΔG was slightly negative. We tended to round the temperature to about the 50°C mark. In a couple cases, PID 105 being a particular case, the use of $\Delta G=0$ fails because the reaction as written always has a positive ΔG, so no temperature can be assigned. Second, particular reactions occur across many cycles. One example reaction would be

$$H_2SO_4 = H_2O + SO_2 + 1/2\ O_2$$
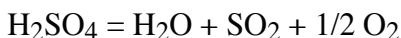
This reaction is reported at 850°C in three cycle, 900°C in another two cycles, 950°C in a third cycle, etc. The variation in temperature reflects the equilibrium composition desired by each author as "best". For simplicity in our work, this particular reaction has been assigned 850°C across all the cycles, in spite of the particular temperature given by the author. Third, cycles may be reported as an aqueous electrolysis, but without a temperature associated. We assigned a value of 25°C to these electrolyses unless otherwise stated. Any user of this compilation of cycle data must keep in mind the temperatures are probably "correct" to ±50°C, and the original literature should be obtained.

Second, we decided to name the cycles by the chemical elements or molecules prominent in the cycle. First, we found that many long standing names were of little utility. As one example, GE-Beulah or GE-Catherine tells us nothing about the cycles. Our names are "new" to the thermochemical hydrogen community. Second, we have merged duplicate cycles under one cycle name, so many longstanding names have disappeared in this merger. The names "Westinghouse" and "GA 22", and some other cycles, are now subsumed under the name "Hybrid sulfur". Third, we have also appended the label "hybrid" to the name as needed, so one can immediately know if the cycle contains an electrolysis. As of this writing, some cycles are still ambiguous to us, whether they require electrolysis or not. The sulfate cycles, which have the reaction

$$MO + SO_2 + H_2O = MSO_4 + H_2$$
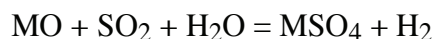
are one set where it is not clear from our literature if electrolysis is necessary. Some info has come to us written (ambiguously) as above, and other literature has asserted this reaction performed without electrolysis makes insignificant H_2, but rather makes other products. The absence of the term "hybrid" in the name does not necessarily mean the cycle does not involve electrolysis! The presence of the term "hybrid" in the name clearly asserts the cycle does involve electrolysis.

Third, the cycle equations have been written in a particular manner for consistency, and so the database software can automatically indicate the presence of a given reaction in several cycles. Products of O_2, H_2 and H_2O are written last in a chemical sequence. The remaining chemicals are written in alphabetical order, as alphabetized by the chemical formula. The equation is written as

$$2\ NaI + 2NH_3(g) + CO_2(g) + H_2O(l) = Na_2CO_3 + 2NH_4I(l)$$
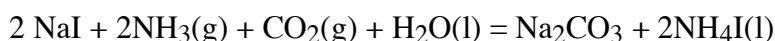
which shows that "sodium iodide" comes before "ammonia", because Na comes before NH, regardless of the language spoken. We wrote all the equations with whole number coefficients, and then used the "multiplier" to weight the equation relative to other equations, so as to add up to

$$H_2O = H_2 + 1/2\ O_2$$
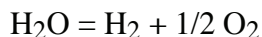
with the formation of one mole of H_2. This last criterion means than in cycles where only one step evolves O_2, the multiplier for that step is always 0.50.

Fourth, we have tried to write the equations with the phases of the compound at the reaction temperature, but in some cases writing the phase is problematic. As one example, the Chemical Rubber Handbook (CRC) lists the melting point of CdO as "d 900°C", as if the compound decomposes at 900°C [2]. PID 5 (Hybrid Cadmium) and PID 182 (Cadmium Carbonate) show a decomposition of CdO(g) at 1200°C. PID 147 (Cadmium Sulfate) lists the formation of CdO (phase unspecified) at 1000°C. The same CRC lists a sublimation temperature for CdO as 1559°C! Lange's Handbook of Chemistry reports a melting point of CdO of 1540°C, with no boiling point [3]. HSC chemistry 5.0 (HSC) reports no melting point, but a boiling point of 1559°C [4]. (So, did CdO decompose at 900°C, or 1200°C, or is CdO(s) still present at 1559°C??) In this particular case, we did not resolve "what is the phase" at the reported temperature, although we suspect the CRC decomposition temperature is incorrect.

Fifth, in the screening, we did no thermodynamic assessment whether the reactions as written occur or not. In trying to assess the temperature of reactions by looking at ΔG, we would occasionally find the reaction has no $\Delta G < 0$ at any reasonable temperature. For instance, PID 105 lists a reaction of ethylene with Mn_2O_3, which always has a very positive ΔG at all temperatures 0-3000°C, but the author did not give a temperature. In PID 202, the reaction of CO and H2 is given at 250°C, but at 250°C, ΔG = +6.4 kcal at standard states. In the same PID, there is a reaction at 100°C, of formaldehyde with H_2 to make methane and oxygen, yet this reaction has a very positive ΔG at all temperatures. The reaction makes no sense, evolving O_2, when O_2 wants to burn hydrocarbons like methane! We have left the cycles in our database for

the sake of completeness in Phase 1, with the temperature quoted by the author. Any users should not consider the presence of a cycle in this compilation as evidence that the cycle is reasonable!! Cycles which moved into Phase 2 did receive a thermodynamic assessment, and such bogus cycles received zero efficiency.

Lastly, we wish to alert any users of this compilation to perform their own thermodynamic assessment carefully. Many cycles found in the literature seem to be based only on as assessment $X \rightarrow Y + H_2$ (or O_2 products) and ΔG for the reaction is negative. Yet there may be competing reactions $X \rightarrow Z$ (no H_2) which are more thermodynamically stable. A global calculation of the reaction and ΔG, with all possible products being assessed, would reveal that Z is made in preference to $Y + H_2$, and the ability of the cycle to make H_2 must be challenged. At this point, the kinetics of the reaction must be evaluated in the lab, to see if $Y + H_2$ is formed rapidly, rather than forming Z. If Z is formed, the cycle does not work.

As one example of the above issue, PID 131 shows the decomposition reaction at 1100°C

$$MnSO_4 = MnO + SO_2 + O_2$$

If the yield of MnO is 100%, the cycle has a particular efficiency. But the global thermodynamic calculation shows at 1100°C that Mn_2O_3 and Mn_3O_4 are significant products. In effect, MnO + O_2 reacted to make higher oxidation state manganese oxides, thereby consuming the O_2. The consumption of oxygen severely diminishes the efficiency of the cycle. The global calculation shows than MnO is a more significant product at 1500°C, so our Phase 2 analysis was performed at 1500°C in order to make the cycle more efficient than at 1100°C.

As a second example of the necessity of doing the global calculation, in looking at all the sulfate cycles, there is tacitly a reaction:

$$SO_2 + 2H_2O(l) = H_2SO_4(aq) + H_2(g)$$
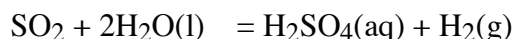
This reaction has a slightly positive ΔG. In this reaction, sulfur is oxidized from +4 to +6, and H+ is reduced to H_2. The presence of a metal oxide MO forming MSO_4 creates a reaction with a negative ΔG. In looking over the entire database of cycles, one sees a variety of products, usually reduced sulfur such as S or sulfide. One can ask "does H_2 reduce SO_2 to S and water, or sulfide and water?" A global thermodynamic calculation shows that the reaction forming H_2

$$MO + SO_2 + H_2O = MSO_4 + H_2(g)$$

has a less negative ΔG than the ΔG for the reaction

$$4MO + 4SO_2 = 3MSO_4 + MS$$
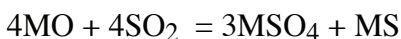
The formation of MS (CaS, BaS, CdS, …) is thermodynamically desired. Only lab work will demonstrate if the formation of H_2 is faster, and the H_2 can be removed from the system before reaction with SO_2. Anyone using this compilation should check for these alternative reaction

paths in a global thermodynamic calculation. One should not assume the presence of a cycle in this compilation means the reactions have all been demonstrated in the lab.

2.5. Results of Phase 1 Scoring

2.5.1. Phase 1 cycles passed to Phase 2

Table 2 gives the cycles which passed from Phase 1 into Phase 2. The actual point score for each cycle is irrelevant for the Phase 2 analysis. A Phase 1 score of 42 for PID A does not make it "worse" than a score of 50 for PID B. Both PID A and PID B had scores greater than 40 and pass into Phase 2. The Phase 1 score has no influence on the Phase 2 assessments.

2.5.2. Analysis and patterns to Phase 1 winners

The results of the Phase I analysis were ranked in order to determine a cut-off score to determine which cycles would be included in the Phase 2 analysis. Figure 2 shows the normalized scores for the Standard Tower and Advanced Tower plotted in rank order. The results for the Trough look very similar to the Standard Tower, and the Dish results are similar to those of the Advanced Tower. A cut-off score of 40 was chosen for the Dish and Advanced Tower and 30 for the Trough and Standard Tower. A lower cut-off was used for the lower temperature devices as we wanted some low temperature cycles represented in the analysis and the low temperature cycles inherently must have more steps and more separations, and thus score lower in our analysis. A sensitivity analysis utilizing Monte Carlo analysis and rank correlation methodology, performed by Sandia National Laboratories, indicated that the selected cycles are not highly dependant on the criteria weights and that the Phase 1 screening process is robust and generally accurate in determining the best cycles for further analysis.
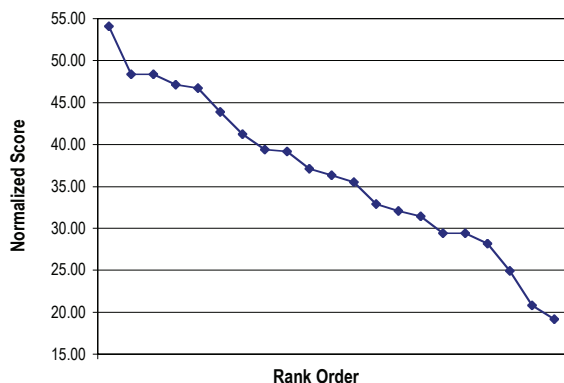

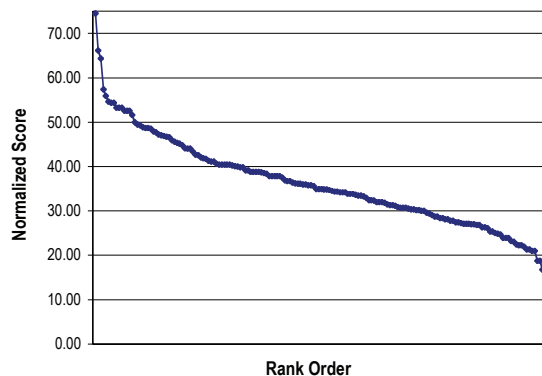Fig. 2. (a) Scores for standard tower.　　　　Fig. 2. (b) Scores for advanced tower.

3. PHASE 2 ANALYSIS

The cycles that passed the filter of Phase 1 screening were further analyzed and screened in Phase 2. The goal was not, as in Phase 1, to "weed out" cycles with low probability of success, but rather, to pick those cycles with a high probability of economic hydrogen production. As the cost of collecting solar energy is rather high, we expect the economics of solar hydrogen production to be dominated by the cost of solar energy. If the capital and operating cost of the chemical plant are small, compared with the capital and operating costs of the solar energy

collection facility, lowest cost hydrogen will originate from the process that has the lowest energy requirement per unit of hydrogen produced. So the Phase 2 assessment focused on the thermal energy efficiency of each cycle, which is equivalent to the energy requirement per unit of hydrogen produced.

3.1. Phase 2 screening procedure

The Phase 2 screening that was applied to those cycles remaining after Phase 1 was done in such a way as to analyze each cycle under the most favorable assumptions, while not wasting resources on cycles that could not possibly compete. A decision tree of the evaluation process is given in Fig. 3. Each cycle was first evaluated for thermodynamic feasibility. The Gibbs free energy of each step was analyzed over a wide temperature range. The quoted temperature was used as a guide, but if the reaction was more favorable at another temperature, we wanted to use the most favorable temperature. If necessary, and possible, an electrochemical step was introduced for steps with large positive Gibbs free energies.

The calculation of thermal efficiency was defined as

$$\eta = \frac{-\Delta H^{\circ}_{25^{\circ}C}(H_2O)}{Q_{hot} + \dfrac{W_s + \Delta G^{\circ}_T + RT\ln\left(\dfrac{\prod_p a_p^{n_p}}{\prod_r a_r^{n_r}}\right) + nFE_{OV}}{0.5}}$$

All work was done using the higher heating value (hhv) to be consistent with historical thermochemical watersplitting work. The tabulated results also include efficiencies based on the lower heating value (lhv) of hydrogen, as mandated by the new hydrogen assessment (H$_2$A) methodology devised by the Department of Energy. Here, $\Delta H_{25C}(H_2O)$ is the higher heating value for water (the heat of formation of liquid water at 25 C), and Q_{hot} is the total high temperature heat required from the solar heat source, W_s is the net amount of shaft work and pumping power done with electric power. The next three terms in the denominator involve the electrical energy cost for the electrolysis in a hybrid cycle: ΔG_T is the thermodynamic energy of the electrolytic reaction under standard conditions, the RTln() term corrects for the solution concentrations, and the nFE$_{OV}$ term corresponds to the overvoltage needed (0.2 V assumed for no membrane separator, or 0.4 V for a hybrid with a membrane separator). The factor of 0.5 assumes 50% efficient generation of electricity from other energy sources to perform the electrolysis and pumping.

A preliminary process flowsheet was generated for each feasible cycle. The flowsheet included calculations of all thermal energy inputs, any heat recuperation and any significant work or electrical energy inputs. All flowsheets were calculated on the basis of the production of one mole of hydrogen so that the energy requirements can be directly compared.
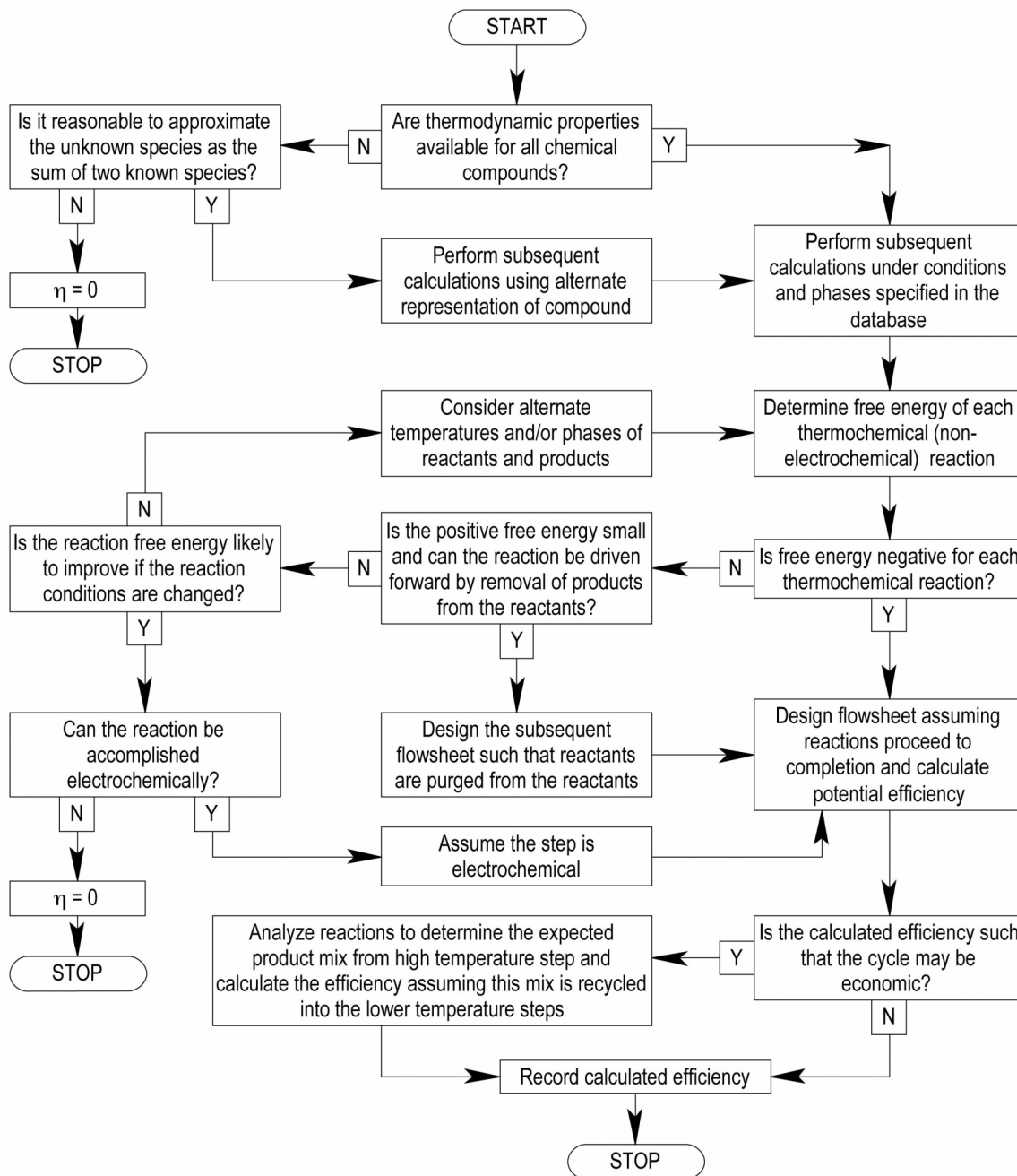
Fig. 3. Proceduree used to determine extent of calculations.

A few cycles had been extensively studied in the past. For these cycles the level of analysis that we could have applied would pale in significance. In these cases we either used previously published results or updated the published results. We were able to update sulfuric acid cycles as we have access to a particularly efficient sulfuric acid concentration and decomposition flowsheet, which was not available when the previous studies were carried out.

3.2. Phase 2 screening results

Table 2 lists the 67 cycles evaluated in Phase 2, with the assessed energy efficiency. There is a tendency to want to express the energy requirement in terms of an efficiency but this requires a defining an energy value for hydrogen. For the first 40 years of thermochemical hydrogen research there was a common definition of the energy value of hydrogen derived from the standard heat of formation of water, $\Delta H^o_{298.15}(H_2O)$. This value can be measured calorimetrically and is probably the most accurately determined measurable quantity in all of chemical thermodynamics. This number is also known as the higher heating value of hydrogen or HHV. Efficiency can also be defined in terms of the lower heating value of hydrogen. The lower heating value is a derived heat of formation of water in a hypothetical state of 1 atm pressure at 25°C. Recently the DOE H2A program has decided that, for consistency within the U.S. hydrogen program, all efficiencies should be given in terms of lower heating value. To be consistent with both the DOE directive and for comparison with the historical work, both values are given in Table 2.

3.3. Conclusions of Phase 2 screening effort

Table 3 lists the cycles that rated highest in our phase 2 analysis along with energy required to produce both 1 mole and 1 kg of hydrogen. These are the cycles which had thermal efficiencies greater than 40% (hhv). These cycles fall into several groups as indicated. Not surprising, the cycles that are actively being pursued by the nuclear hydrogen program, Hybrid Sulfur, Sulfur-Iodine and Hybrid Copper Chloride made good showings in our analysis. Other cycles deemed applicable to the use of concentrated solar energy, include two and three step metal oxide decomposition process involving either metal vapor or metal oxide products, cycles involving decomposition of metal sulfates or carbonates, and a cycle involving sulfur in four different valence states.

Additional experimental work in needed on the processes that are not presently under the aegis of the nuclear hydrogen program. The zinc oxide and sodium-manganese cycles are currently being investigated at the University of Colorado. The low temperature step of the hybrid cadmium oxide cycle has been studied in the past and there have been many superficial studies of various ferrite processes. The multivalent sulfur and cadmium carbonate cycle have not been investigated, but appear to be viable. The sulfate processes are somewhat unique in that there is still a question as to their overall viability. In general, sulfates are not the lowest free energy states; but sulfates may be kinetically favored over the lower energy sulfite and elemental sulfur states, in which case these cycles may be viable.

Appendix 2 gives a brief summary of the thermal efficiency assessments for all the cycles in Phase 2.

Table 2. Thermal Efficiencies and Heat Requirements for the Cycles Assessed in Phase 2

PID	Cycle name	efficiency LHV (0.846*HHV)	efficiency HHV
1	Sulfur-Iodine	38.1	45 (a)
2	Nickel-Manganese Ferrite	44.0	52 (b)
4	Iron Chloride-1	0.0	0.0
5	Hybrid Cadmium	45.1	53.3
6	Zinc-Zinc Oxide	45.0	53.2
7	Iron oxide	42.3	50.0
9	Manganese-Carbon	0.0	0.0
14	Sodium-Manganese-1	0.0	0.0
16	Vanadium Oxychloride-1	0.0	0.0
22	Iron Chloride-4	31.0	36.6
23	Manganese Chloride-1	26.6	31.4
24	Hybrid Lithium Nitrate	32.8	38.8
25	Cesium Hydroxide	0.0	0.0
26	Copper Magnesium Chloride	17.4	20.6
36	Cesium Amalgam-1	0.0	0.0
49	Uranium Carbonate-1	0.0	0.0
50	Lithium Manganese	0.0	0.0
51	Potassium Peroxide	< 23.5	< 27.8
53	Hybrid Chlorine	21.6	25.5
56	Copper Chloride	29.2	34.5
61	Sodium-Iron	22.8	27.0
62	Iron Bromide	< 27.7	< 32.8
63	Iron-Carbon Monoxide-2	0.0	0.0
67	Hybrid Sulfur	43.1	50.9 (a)
68	Arsenic-Ammonium Iodide	6.7	7.9
70	Hybrid Sulfur-Bromine	33.4	39.5
72	Calcium-Iron Bromide-2	33.8	40.0
82	Manganese-Magnesium Iodide-1	< 32.2	< 38.1
91	Carbon-Scandium Bromide	0.0	0.0
93	Tungsten-Aluminum Bromide	0.0	0.0
103	Cerium Chloride	18.0	21.3
104	Magnesium-Cerium Chloride	15.1	17.9
105	Manganese-Ethane-Ethylene	0.0	0.0
106	High temperature electrolysis	49.1	58.0
110	Sodium Manganese-3	50.0	59.1
111	Sodium-Manganese Ferrite-1	0.0	0.0
112	Iron Chloride-9	0.0	0.0
114	Hybrid Nitrogen-Iodine	< 28.2	< 33.3
124	Copper Sulfate-1	0.0	0.0

Table 2 Continued

PID	Cycle name	efficiency	efficiency
126	Cesium Amalgum-2	0.0	0.0
129	Magnesium Sulfate	5.1	6 (c)
131	Manganese Sulfate	35.4	41.8 (c)
132	Ferrous Sulfate-3	14.4	17 (c)
133	Ferrous Sulfate-4	0.0	0 (c)
134	Cobalt Sulfate	29.9	35.3 (c)
147	Cadmium Sulfate	46.5	55 (c)
149	Barium-Molybdenum Sulfate	39.5	46.7 (c)
151	Carbon-Sulfur	0.0	0.0
152	Iron-Zinc	< 19.9	< 23.5
153	Sodium-Manganese Ferrite-2	0.0	0.0
154	Sodium Ferrite	na	na
160	Arsenic-Iodine	< 21.2	< 25
162	Uranium Carbonate-2	0.0	0.0
163	Manganese Carbonate	0.0	0.0
177	Lead Chloride	0.0	0.0
182	Cadmium Carbonate	44.3	52.4
184	Hybrid Antimony-Bromine	30.6	36.2
185	Hybrid Cobalt Bromide-2	21.7	25.6
191	Hybrid Copper Chloride	41.6	49.2
193	Multivalent sulfur-3	35.5	42.2
194	Zinc-Manganese Ferrite	44.0	52(b,d)
196	Sodium Carbonate-Iodate	0.0	0.0
198	Calcium Bromide	0.0	0.0
199	Iron Chloride-11	< 16.9	< 20(a)
200	Iron Chloride-12	16.9	20(a)
201	Carbon Oxides	31.4	37.1
202	Methanol-Formaldehyde	0.0	0.0

(a) efficiency calculated from previous studies

(b) efficiency estimated, limited thermodynamic data

(c) efficiency calculated presuming cycle is not a hybrid

(d) assumed same as PID 2

 na not assessable

Table 3. Heat requirements of top rated cycles

PID #	Cycle class and name	kJ input per mole H_2	MJ input per kg H_2	Efficiency (hhv) %	Efficiency (lhv) %
	Sulfuric acid				
67	Hybrid sulfur	560	278	51	43.1
1	Sulfur-iodine	635	315	45	38.1
193	Multivalent sulfur	681	338	42	35.5
	Metal sulfate				
147	Cadmium sulfate	520	258	55	46.5
149	Barium sulfate	608	302	47	39.8
131	Manganese sulfate	681	338	42	35.5
	Volatile metal				
5	Hybrid cadmium	539	267	53	44.8
182	Cadmium carbonate	550	273	52	44
6	Zinc oxide	537	266	53.2	45
	Metal oxide				
110	Sodium Manganese-3	484	240	59.1	50
2	Nickel-Manganese Ferrite	550	273	52	44
194	Zinc-Manganese Ferrite	550	273	52	44
7	Iron Oxide	572	286	50	42.3
	Other				
191	Hybrid copper chloride-2	583	289	49	41.5

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APPENDIX 1

This appendix list each cycle remaining in the database after removal of duplicates. Tabulated information includes:

PID #   The process identification number is a unique number assigned to a cycle when it was first entered into the database. If a cycle was later found to be a duplicate of another cycle in the database, it was removed from the database. The PID numbers of removed cycles are not reassigned.

Name   Each cycle was assigned a unique descriptive name. If the cycle aleady had a descriptive name, that name was retained. Where the same descriptive name fits several cycles an index number was appended. The term "hybrid" was prefixed to the name of an electrochemical step. Some of the cycles were previously known a by non-descriptive name, or even by several different non-descriptive names. Alternative names were retained in the database for search purposes.

T (C)   The temperature given in the primary sources for each chemical reaction. When a chemical reaction is common to several cycles multiple temperatures may be indicated in the various references, but only one temperature is indicated throughout the database. If our suggested analysis indicated that the reaction is infeasible at the indicated temperature by another temperature is feasible, the feasible temperature may be substituted.

Multiplier   Each chemical reaction is listed in the database in its simplest form. The multiplier is the number of times the simple reaction must be taken to make the overall cycle balance to provide one mole of hydrogen.

Reaction   A chemical reaction of the cycle given in its simplest form.

Trough   The normalized score of the cycle using the criteria given in Table 1.

Tower   The score of the cycle normalized using the criteria given in Table 1 of the report for a standard tower heat source.

Dish   The normalized score for the cycle using the criteria given in Table 1 of the report for a dish heat source.

Adv tower   The normalized score for the cycle using the criteria given in Table 1 of the report for an advanced tower heat source.

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
1	Sulfur-Iodine	850	0.50	$2H2SO4(g) = 2SO2(g) + 2H2O(g) + O2(g)$	41.92	41.92	53.46	61.15
		300	1.00	$2HI(g) = I2(g) + H2(g)$				
		100	1.00	$I2(a) + SO2(a) + 2H2O = 2HI(a) + H2SO4(a)$				
2	Nickel-Manganese Ferrite	800	0.50	$NiMnFe4O6 + 2H2O = NiMnFe4O8 + 2H2(g)$	50.19	50.19	69.42	67.5
		800	0.50	$NiMnFe4O8 = NiMnFe4O6 + O2(g)$				
3	Mercury-Calcium Bromide-1	200	1.00	$2HBr(g) + Hg(l) = HgBr2 + H2(g)$	6.92	6.92	12.69	26.15
		500	0.50	$2HgO(g) = 2Hg(g) + O2(g)$				
		750	1.00	$CaBr2(l) + H2O = CaO + 2HBr(g)$				
		25	1.00	$CaO + HgBr2 = CaBr2 + HgO$				
4	Iron Chloride-1	420	1.50	$2FeCl3(g) = Cl2(g) + 2FeCl2$	32.69	40.38	34.62	44.23
		150	0.50	$3Cl2(g) + 2Fe3O4 + 12HCl(g) = 6FeCl3 + 6H2O + O2(g)$				
		650	1.00	$3FeCl2 + 4H2O(g) = Fe3O4 + 6HCl(g) + H2(g)$				
5	Hybrid Cadmium	1200	0.50	$2CdO(s) = 2Cd(g) + O2(g)$	37.12	37.12	56.35	52.5
		25	1.00	$Cd + 2H2O(l) = Cd(OH)2 + H2(g)$ (0.02 v)				
		375	1.00	$Cd(OH)2(g) = CdO + H2O(g)$				
6	Zinc-Zinc Oxide	2200	0.50	$2ZnO(l) = 2Zn(g) + O2(g)$	55.58	55.58	57.5	55.58
		900	1.00	$Zn + H2O(g) = ZnO + H2(g)$				
7	Iron Oxide	2200	0.50	$2Fe3O4(l) = 6FeO(l) + O2(g)$	57.31	57.31	59.23	57.31
		700	1.00	$3FeO + H2O(g) = Fe3O4 + H2(g)$				
9	Manganese-Carbon	977	0.50	$6Mn2O3 = 4Mn3O4 + O2(g)$	33.08	33.08	50.38	52.31
		700	1.00	$C + H2O(g) = CO(g) + H2(g)$				
		700	1.00	$CO(g) + 2Mn3O4 = C + 3Mn2O3$				
10	Iron Chloride-2	610	0.50	$2Cl2(g) + 2H2O(g) = 4HCl(g) + O2(g)$	10.38	10.38	16.15	27.69
		420	1.00	$2FeCl3(g) = Cl2(g) + 2FeCl2$				
		155	1.00	$2FeO + H2O(g) = Fe2O3 + H2(g)$				
		120	1.00	$Fe2O3 + 6HCl(g) = 2FeCl3 + 3H2O(g)$				
		739	2.00	$FeCl2(l) + H2O(g) = FeO + 2HCl(g)$				
11	Mercury-Calcium Bromide-2	120	1.00	$2HBr(g) + Hg2Br2 = 2HgBr2 + H2(g)$	9.23	9.23	15	26.54
		500	0.50	$2HgO(g) = 2Hg(g) + O2(g)$				
		200	1.00	$Ca(OH)2 + HgBr2 = CaBr2 + HgO + H2O(g)$				
		730	1.00	$CaBr2 + 2H2O(g) = Ca(OH)2 + 2HBr(g)$				
		120	1.00	$Hg(l) + HgBr2 = Hg2Br2$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
12	Copper-Bromine	100	2.00	$CuBr_2 + Ca(OH)_2 = CuO + CaBr_2(ia) + H_2O(g)$	17.69	17.69	31.15	36.92
		900	0.50	$4CuO = 2Cu_2O + O_2(g)$				
		730	2.00	$CaBr_2 + 2H_2O(g) = Ca(OH)_2 + 2HBr(g)$				
		100	1.00	$Cu_2O + 4HBr(g) = 2CuBr_2 + H_2(g) + H_2O(g)$				
13	Mercury-Strontium Bromide	200	1.00	$2HBr(g) + Hg(l) = HgBr_2 + H_2(g)$	14.23	14.23	23.85	33.46
		500	0.50	$2HgBr_2(g) + 2SrO = 2Hg(g) + 2SrBr_2 + O_2(g)$				
		800	1.00	$SrBr_2(l) + H_2O(g) = 2HBr(g) + SrO$				
14	Sodium-Manganese-1	100	1.00	$2Na_2O.MnO_2 + H_2O = 2NaOH(a) + MnO_2$	38.65	38.65	48.27	57.88
		487	0.50	$4MnO_2(s) = 2Mn_2O_3(s) + O_2(g)$				
		800	1.00	$Mn_2O_3 + 4NaOH(l) = 2Na_2O.MnO_2 + H_2(g) + H_2O(g)$				
15	Sodium-Manganese-2	487	0.50	$4MnO_2(s) = 2Mn_2O_3(s) + O_2(g)$	30	30	41.54	49.23
		450	1.00	$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$				
		850	1.00	$Mn_2O_3 + 2Na_2CO_3 = CO(g) + CO_2(g) + 2Na_2O.MnO_2$				
		100	2.00	$Na_2O.MnO_2 + CO_2(g) + H_2O = MnO_2 + Na_2CO_3$				
16	Vanadium Oxychloride-1	610	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	31.73	31.73	41.35	50.96
		170	1.00	$2VOCl_2 + 2HCl(g) = 2VOCl_3(g) + H_2(g)$				
		200	1.00	$2VOCl_3(g) = Cl_2(g) + 2VOCl_2$				
17	Iron-Chlorine-Sulfur	610	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	16.73	16.73	26.35	35.96
		100	1.00	$2FeCl_2 + 2HCl(g) + S = 2FeCl_3 + H_2S(g)$				
		420	1.00	$2FeCl_3(g) = Cl_2(g) + 2FeCl_2$				
		800	0.50	$2H_2S(g) = S_2(g) + 2H_2(g)$				
18	Mercury-Calcium-Bromide-3	200	0.00	$2HBr(g) + Hg(l) = HgBr_2 + H_2(g)$	4.62	4.62	18.08	23.85
		500	0.50	$2HgO(g) = 2Hg(g) + O_2(g)$				
		600	1.00	$CaBr_2 + CO_2(g) + H_2O(g) = CaCO_3 + 2HBr(g)$				
		900	1.00	$CaCO_3 = CaO + CO_2(g)$				
		25	1.00	$CaO + HgBr_2 = CaBr_2 + HgO$				
19	Chromium-Iron-Chlorine	610	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	27.12	27.12	36.73	46.35
		170	1.00	$2CrCl_2 + 2HCl(g) = 2CrCl_3 + H_2(g)$				
		700	0.00	$2CrCl_3 + 2FeCl_2(l) = 2CrCl_2 + 2FeCl_3(g)$				
		420	0.00	$2FeCl_3(g) = Cl_2(g) + 2FeCl_2$				
20	Chromium-Copper-Chlorine	800	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	10.58	10.58	20.19	29.81
		170	1.00	$2CrCl_2 + 2HCl(l) = 2CrCl_3 + H_2(g)$				
		700	1.00	$2CrCl_3 + 2FeCl_2(l) = 2CrCl_2 + 2FeCl_3(g)$				
		500	1.00	$2CuCl_2 = 2CuCl(l) + Cl_2(g)$				
		150	1.00	$CuCl + FeCl_3 = CuCl_2 + FeCl_2$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
21	Iron Chloride-3	420	1.50	$2FeCl3(l) = Cl2(g) + 2FeCl2$	12.31	12.31	31.54	29.62
		650	1.00	$3FeCl2 + 4H2O(g) = Fe3O4 + 6HCl(g) + H2(g)$				
		350	0.25	$4Fe3O4 + O2(g) = 6Fe2O3$				
		1000	0.25	$6Cl2(g) + 2Fe2O3 = 4FeCl3(g) + 3O2(g)$				
		120	1.00	$Fe2O3 + 6HCl(a) = 2FeCl3(a) + 3H2O(l)$				
22	Iron Chloride-4	1000	0.75	$2Fe2O3 + 6Cl2(g) = 4FeCl3(g) + 3O2(g)$	31.54	31.54	50.77	48.85
		420	1.50	$2FeCl3(g) = Cl2(g) + 2FeCl2$				
		650	1.00	$3FeCl2 + 4H2O(g) = Fe3O4 + 6HCl(g) + H2(g)$				
		350	0.25	$4Fe3O4 + O2(g) = 6Fe2O3$				
		400	1.50	$4HCl(g) + O2(g) = 2Cl2(g) + 2H2O(g)$				
23	Manganese Chloride-1	700	0.00	$3MnCl2 + 4H2O(g) = Mn3O4 + 6HCl(g) + H2(g)$	25.77	25.77	39.23	45
		900	0.50	$3MnO2 = Mn3O4 + O2(g)$				
		100	0.50	$12HCl(a) + 3Mn3O4 = 6MnCl2(a) + 3MnO2 + 6H2O(l)$				
24	Hybrid Lithium Nitrate	300	1.00	$2HI(g) = I2(g) + H2(g)$	29.23	19.62	13.85	13.85
		427	0.50	$2LiNO3(l) = 2LiNO2(l) + O2(g)$				
		27	1.00	$I2(a) + LiNO2(ia) + H2O = 2HI(ia) + LiNO3(ia)$				
25	Cesium Hydroxide	450	1.00	$2Cs(l) + 2H2O(g) = 2CsOH(l) + H2(g)$	15.38	15.38	26.92	23.08
		2700	0.50	$2Cs2O(l) = 4Cs(g) + O2(g)$ (T = 1642 C; 2700 if Cs(l))				
		450	0.50	$4CsO2(s) = 2Cs2O + 3O2(g)$				
		250	0.50	$4CsOH(a) + 3O2(g) = 4CsO2 + 2H2O(g)$				
26	Copper Magnesium Chloride	25	0.50	$2Cl2(g) + 2Mg(OH)2(s) = 2MgCl2(s) + 2H2O(l) + O2(g)$	21.35	30.96	11.73	13.65
		100	1.00	$2Cu(s) + 2HCl(g) = 2CuCl(s) + H2(g)$				
		100	2.00	$2CuCl(s) = Cu(s) + CuCl2(s)$				
		500	1.00	$2CuCl2(s) = 2CuCl(l) + Cl2(g)$				
		450	1.00	$MgCl2(s) + 2H2O(g) = 2HCl(g) + Mg(OH)2(l)$				
27	Ferrous Sulfate-1	800	0.50	$2Fe3O4(s) + 6FeSO4(g) = 6Fe2O3(s) + 6SO2(g) + O2(g)$	28.46	28.46	38.08	47.69
		700	1.00	$3FeO(s) + H2O(g) = Fe3O4(s) + H2(g)$				
		200	3.00	$Fe2O3(s) + SO2(g) = FeO(s) + FeSO4(g)$				

A1-4

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
28	Iron-Magnesium Chloride	25	0.50	$2Cl_2(g) + 2Mg(OH)_2(s) = 2MgCl_2(a) + 2H_2O(l) + O_2(g)$	13.46	21.15	15.38	25
		420	1.00	$2FeCl_3(g) = Cl_2(g) + 2FeCl_2(s)$				
		650	1.00	$3FeCl_2(s) + 4H_2O(g) = Fe_3O_4(s) + 6HCl(g) + H_2(g)$				
		230	1.00	$Fe_3O_4(s) + 8HCl(g) = FeCl_2(s) + 2FeCl_3(s) + 4H_2O(g)$				
		450	1.00	$MgCl_2(a) + 2H_2O(g) = 2HCl(g) + Mg(OH)_2(l)$				
29	Alkali Nickel Iodide	650	0.17	$2KIO_3(g) = 2KI(s) + 3O_2(g)$	6.92	6.92	10.77	22.31
		150	1.00	$2HI(g) + Ni(s) = NiI_2(s) + H_2(g)$				
		190	0.33	$3I_2(g) + 6LiOH(s) = 5LiI(s) + LiIO_3(g) + 3H_2O(g)$				
		0	0.33	$KI(s) + LiIO_3(g) = KIO_3(g) + LiI(s)$				
		600	2.00	$LiI(l) + H_2O(g) = HI(g) + LiOH(l)$				
		700	1.00	$NiI_2(s) = I_2(g) + Ni(s)$				
30	Ferrous Sulfate-2	800	0.50	$2SO_3(g) = 2SO_2(g) + O_2(g)$	30.19	30.19	43.65	49.42
		25	0.25	$3Fe_2O_3(s) + SO_2(g) = 2Fe_3O_4(s) + SO_3(l)$				
		25	0.50	$Fe_3O_4(s) + 3SO_2(g) + 2H_2O(l) = 3FeSO_4(g) + 2H_2(g)$				
		900	0.75	$2FeSO_4(g) = Fe_2O_3(s) + SO_2(g) + SO_3(g)$				
31	Iron Chloride-5	420	1.00	$2FeCl_3(g) = Cl_2(g) + 2FeCl_2(s)$	11.92	11.92	31.15	29.23
		500	0.67	$3Fe(s) + 4H_2O(g) = Fe_3O_4(s) + 4H_2(g)$				
		400	1.00	$4HCl(g) + O_2(g) = 2Cl_2(g) + 2H_2O(g)$				
		1000	0.33	$9Cl_2(g) + 2Fe_3O_4(s) = 6FeCl_3(g) + 4O_2(g)$				
		1000	2.00	$FeCl_2(l) + H_2(g) = Fe(s) + 2HCl(g)$				
32	Vanadium Chloride	610	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	14.81	14.81	18.65	30.19
		25	1.00	$2HCl(g) + 2VCl_2(s) = 2VCl_3(s) + H_2(g)$				
		700	2.00	$2VCl_3(l) = VCl_4(l) + VCl_2(s)$				
		25	1.00	$2VCl_4(l) = Cl_2(g) + 2VCl_3(s)$				
33	Chromium Chloride	610	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	21.73	21.73	31.35	40.96
		170	1.00	$2CrCl_2(s) + 2HCl(g) = 2CrCl_3(s) + H_2(g)$				
		800	1.00	$2CrCl_3(s) = 2CrCl_2(s) + Cl_2(g)$				
34	Vanadium Selenium	500	0.50	$2V_2O_5(s) = 2V_2O_4(s) + O_2(g)$	11.15	11.15	15	26.54
		700	0.50	$4KOH(l) + 3Se(g) = 2K_2Se(s) + SeO_2(l) + 2H_2O(g)$				
		200	1.00	$H_2Se(g) = Se(s) + H_2(g)$				
		100	1.00	$K_2Se(a) + 2H_2O(l) = 2KOH(s) + H_2Se(g)$				
		327	0.50	$SeO_2(s) + 2V_2O_4(s) = Se(l) + 2V_2O_5(s)$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
35	Magnesium Selenide	500	0.13	$2Mg(OH)2(l) + 4Se(l) = 2H2Se(g) + MgSe + MgSeO4$	14.42	14.42	33.65	31.73
		200	0.50	$H2Se(g) = Se(s) + H2(g)$				
		100	0.25	$MgSe + 2H2O(l) = H2Se(g) + Mg(OH)2 (s)$				
		400	0.13	$MgSe + 4H2O(g) = MgSeO4 + 4H2(g)$				
		1100	0.25	$MgSeO4 = MgSe + 2O2(g)$				
36	Cesium Amalgam-1	410	1.00	$2CsOH(l) = Cs2O(s) + H2O(g)$	29.04	40.58	27.12	34.81
		500	0.50	$2HgO(l) = 2Hg(g) + O2(g)$				
		600	1.00	$Cs2Hg + 2H2O(g) = 2CsOH(l) + Hg(g) + H2(g)$				
		300	1.00	$Cs2O(s) + 2Hg(l) = Cs2Hg + HgO(s)$				
37	Methanol-Arsenic	25	0.50	$As2O3(s) + As2O5(s) = 2As2O4(g)$	15.96	15.96	19.81	31.35
		227	1.00	$As2O4(g) + CH3OH(g) = As2O5(s) + CH4(g)$				
		700	0.50	$As2O5(l) = As2O3(l) + O2(g)$				
		700	1.00	$CH4(g) + H2O(g) = CO(g) + 3H2(g)$				
		230	1.00	$CO(g) + 2H2(g) = CH3OH(g)$				
38	Europium-Strontium Iodide	390	1.00	$2EuO(s) + H2O(g) = Eu2O3(s) + H2(g)$	21.15	21.15	23.08	21.15
		323	0.50	$2I2(g) + 2SrO(s) = 2SrI2(s) + O2(g)$				
		2200	1.00	$Eu2O3(s) + SrI2(l) = 2EuO(l) + SrO(s) + I2(g)$				
40	Iron-Carbon Monoxide-1	315	0.50	$2CO2(g) = 2CO(g) + O2(g)$	21.92	21.92	37.31	41.15
		700	0.50	$3FeO (s) + H2O(g) = Fe3O4(s) + H2(g)$				
		950	0.50	$CO(g) + Fe3O4(s) = CO2(g) + 3FeO(s)$				
		100	0.50	$CO(g) + FeO(s) = CO2(g) + Fe(s)$				
		150	0.50	$Fe(s) + H2O(g) = FeO (s) + H2(g)$				
41	Iron Chloride-6	610	0.50	$2Cl2(g) + 2H2O(g) = 4HCl(g) + O2(g)$	23.08	32.69	21.15	30.77
		600	1.00	$2FeCl2(s) + 2HCl(g) = 2FeCl3(g) + H2(g)$				
		420	1.00	$2FeCl3(g) = Cl2(g) + 2FeCl2(s)$				
42	Tin Oxide	700	0.50	$2SnO (s) = Sn(l) + SnO2(s)$	32.12	32.12	41.73	37.88
		1700	0.50	$2SnO2(l) = 2SnO(g) + O2(g)$				
		400	0.50	$Sn(l) + 2H2O(g) = SnO2(s) + 2H2(g)$				
43	Silver Bromide	477	1.00	$2Ag (s) + 2NH4Br (g) = 2AgBr (l) + 2NH3(g) + H2(g)$	7.69	7.69	13.46	25
		127	1.00	$2NaHCO3 (g) = CO2(g) + Na2CO3 (s) + H2O(g)$				
		727	0.50	$4AgBr (l) + 2Na2CO3(s) = 4Ag (s) + 2CO2(g) + 4NaBr (s) + O2(g)$				
		27	2.00	$CO2(g) + NaBr(a) + NH3(g) + H2O(l) = NaHCO3(g) + NH4Br(l)$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
44	Iodine-Sulfur Trioxide	300	1.00	$2HI(g) = I_2(g) + H_2(g)$	16.92	16.92	26.54	36.15
		800	0.50	$2SO_3(g) = 2SO_2(g) + O_2(g)$				
		100	1.00	$I_2(a) + SO_2(g) + H_2O(l) = 2HI(g) + SO_3(g)$				
45	Nitrogen-Iodine-1	25	1.00	$2KI(s) + 2NH_4NO_3(s) = 2KNO_3(s) + 2NH_4I(l)$	6.92	6.92	10.77	22.31
		500	1.00	$2NH_4I(g) = I_2(g) + 2NH_3(g) + H_2(g)$				
		25	0.50	$4NO_2(g) + 2H_2O(l) + O_2(g) = 4HNO_3(l)$				
		25	2.00	$HNO_3(l) + NH_3(g) = NH_4NO_3(s)$				
		700	1.00	$I_2(g) + 2KNO_3(g) = 2KI(l) + 2NO_2(g) + O_2(g)$				
46	Ferric Sulfate	800	0.50	$2SO_3(g) = 2SO_2(g) + O_2(g)$	10.19	10.19	19.81	29.42
		450	1.00	$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$				
		350	1.00	$CO_2(g) + SO_2(g) + H_2O(g) = CO(g) + H_2SO_4(g)$				
		800	0.33	$Fe_2(SO_4)_3(s) = Fe_2O_3(s) + 3SO_3(g)$				
		50	0.33	$Fe_2O_3(s) + 3H_2SO_4(l) = Fe_2(SO_4)_3(s) + 3H_2O(l)$				
47	Tantalum Chloride	610	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	15.96	15.96	31.35	27.5
		25	1.00	$2HCl(g) + 2TaCl_2(s) = 2TaCl_3(s) + H_2(g)$				
		1400	1.00	$2TaCl_3(g) = Cl_2(g) + 2TaCl_2(g)$				
48	Chromium Bromide	25	1.00	$2CrBr_2(s) + 2HBr(g) = 2CrBr_3(s) + H_2(g)$	17.31	17.31	25	19.23
		1900	1.00	$2CrBr_3(l) = Br_2(g) + 2CrBr_2(g)$				
		850	0.50	$2H_2SO_4(g) = 2SO_2(g) + 2H_2O(g) + O_2(g)$				
		77	1.00	$Br_2(g) + SO_2(g) + 2H_2O(l) = 2HBr(g) + H_2SO_4(l)$				
49	Uranium Carbonate-1	25	1.00	$3CO_2 + U_3O_8(s) + H_2O = 3UO_2CO_3(s) + H_2(g)$	43.65	43.65	47.5	59.04
		250	1.00	$3UO_2CO_3(s) = 3CO_2(g) + 3UO_3(s)$				
		700	0.50	$6UO_3(s) = 2U_3O_8(s) + O_2(g)$				
50	Lithium Manganese	80	1.00	$3Li_2O.Mn_2O_3(s) + 3H_2O = 6LiOH(s) + 3Mn_2O_3(s)$	36.92	36.92	54.23	56.15
		700	1.00	$6LiOH(l) + 2Mn_3O_4(s) = 3Li_2O.Mn_2O_3(s) + H_2(g) + 2H_2O$				
		977	0.50	$6Mn_2O_3(s) = 4Mn_3O_4(s) + O_2(g)$				
51	Potasium Peroxide	725	1.00	$2K(l) + 2KOH(l) = 2K_2O + H_2(g)$	41.35	41.35	50.96	60.58
		825	1.00	$2K_2O = 2K(l) + K_2O_2(l)$				
		125	0.50	$2K_2O_2(s) + 2H_2O = 4KOH(s) + O_2(g)$				
52	Ferrous Sulfate-Iodine	700	1.00	$2FeSO_4(s) + I_2(g) + 2H_2O = 2Fe(OH)SO_4(s) + 2HI$	26.54	26.54	30.38	41.92
		300	1.00	$2HI = I_2(g) + H_2(g)$				
		250	0.50	$4Fe(OH)SO_4(s) = 4FeSO_4(s) + 2H_2O + O_2(g)$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
53	Hybrid Chlorine	800	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	45.38	45.38	55	64.62
		300	1.00	$2HCl = Cl_2(g) + H_2(g)$				
54	Hybrid Mercurous Chloride	800	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	25.77	25.77	35.38	45
		300	1.00	$2HCl + 2Hg(l) = 2HgCl(s) + H_2(g)$				
		500	1.00	$2HgCl(s) = 2Hg(g) + Cl_2(g)$				
55	Hybrid Nitrosyl Chloride	700	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	13.27	13.27	22.88	32.5
		176	1.00	$2FeCl_3(s) + 2NO = 2FeCl_2(s) + 2NOCl(g)$				
		150	1.00	$2NOCl(g) = Cl_2(g) + 2NO(g)$				
		200	1.00	$2FeCl_2(s) + 2HCl = 2FeCl_3(s) + H_2(g)$ electrolysis				
56	Copper Chloride	800	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	30.96	30.96	40.58	50.19
		200	1.00	$2CuCl(s) + 2HCl = 2CuCl_2(s) + H_2(g)$				
		500	1.00	$2CuCl_2(s) = 2CuCl(l) + Cl_2(g)$				
59	Calcium Iodide	700	0.10	$2Ca(IO_3)_2 = 2CaO + 2I_2(g) + 5O_2(g)$	13.85	13.85	33.08	31.15
		300	1.00	$2HI(g) = I_2(g) + H_2(g)$				
		1000	0.20	$5CaI_2(l) + 5H_2O(g) = 5CaO + 10HI(g)$				
		30	0.20	$6CaO + 6I_2 = 5CaI_2 + Ca(IO_3)_2$				
60	Barium Iodide	800	0.50	$2BaCO_3 + 2I_2(g) = 2BaI_2(l) + 2CO_2(g) + O_2(g)$	16.92	16.92	26.54	36.15
		500	1.00	$2NH_4I = I_2(g) + 2NH_3(g) + H_2(g)$				
		25	1.00	$BaI_2 + CO_2(g) + 2NH_3(g) + H_2O = BaCO_3 + 2NH_4I$				
61	Sodium-Iron	1140	1.00	$2Fe_3O_4 + 6NaOH(l) = 3Na_2O.Fe_2O_3 + 2H_2O(g) + H_2(g)$	27.88	27.88	41.35	37.5
		530	1.00	$3Na_2O.Fe_2O_3 + 3H_2O(g) = 3Fe_2O_3 + 6NaOH(l)$				
		1470	0.50	$6Fe_2O_3 = 4Fe_3O_4 + O_2(g)$				
62	Iron Bromide	1000	0.50	$2Br_2(g) + 2H_2O(g) = 4HBr(g) + O_2(g)$	36.92	36.92	56.15	54.23
		600	1.00	$3FeBr_2 + 4H_2O(g) = Fe_3O_4 + 6HBr(g) + H_2(g)$				
		300	1.00	$Fe_3O_4 + 8HBr(g) = Br_2(g) + 3FeBr_2 + 4H_2O(g)$				
63	Iron-Carbon Monoxide-2	1470	0.50	$6Fe_2O_3 = 4Fe_3O_4 + O_2(g)$	34.42	34.42	47.88	44.04
		700	1.00	$C + H_2O(g) = CO(g) + H_2(g)$				
		250	1.00	$CO(g) + 2Fe_3O_4 = C + 3Fe_2O_3$				
64	Copper-Ammonia	700	1.00	$2CuO + I_2(g) = 2CuI(l) + O_2(g)$	31.15	31.15	35	46.54
		500	1.00	$2NH_4I = I_2(g) + 2NH_3(g) + H_2(g)$				
		25	0.50	$4CuI + 4NH_3(g) + 2H_2O(l) + O_2(g) = 4CuO + 4NH_4I$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
65	Sodium-Ammonium Iodide	700	0.50	$2I_2(g) + 2Na_2CO_3 = 2CO_2(g) + 4NaI(g) + O_2(g)$	14.23	14.23	18.08	29.62
		25	1.00	$2NaI + 2NH_3(g) + CO_2(g) + H_2O(l) = Na_2CO_3 + 2NH_4I(l)$				
		500	1.00	$2NH_4I(g) = I_2(g) + 2NH_3(g) + H_2(g)$				
67	Hybrid Sulfur	850	0.50	$2H_2SO_4(g) = 2SO_2(g) + 2H_2O(g) + O_2(g)$	55.77	55.77	71.15	75
		77	1.00	$SO_2(g) + 2H_2O(l) = H_2SO_4(l) + H_2(g)$				
68	Arsenic-Ammonium Iodide	554	0.50	$2(NH_4)H_2AsO_4 = As_2O_3(g) + 2NH_3(g) + 3H_2O(g) + O_2(g)$	21.92	33.46	16.15	20
		500	1.00	$2NH_4I(g) = I_2(g) + 2NH_3(g) + H_2(g)$				
		198	0.50	$As_2O_3 + 2I_2(g) + 6NH_3(g) + 5H_2O(g) = 2(NH_4)H_2AsO_4 + 4NH_4I(l)$				
69	Antimony-Iodine	300	1.00	$2HI(g) = I_2(g) + H_2(g)$	20.58	20.58	39.81	37.88
		5	0.50	$2I_2 + Sb_2O_3 + 2H_2O(l) = 4HI(g) + Sb_2O_5$				
		1000	0.50	$Sb_2O_5 = Sb_2O_3(l) + O_2(g)$				
70	Hybrid Sulfur-Bromine	850	0.50	$2H_2SO_4(g) = 2SO_2(g) + 2H_2O(g) + O_2(g)$	44.04	44.04	55.58	63.27
		77	1.00	$2HBr(ia) = Br_2 + H_2(g)$				
		77	1.00	$Br_2(g) + SO_2(a) + 2H_2O = 2HBr(a) + H_2SO_4(a)$				
71	Iron Chloride-7	800	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	27.31	27.31	36.92	46.54
		420	1.00	$2FeCl_3(g) = Cl_2(g) + 2FeCl_2$				
		650	1.00	$3FeCl_2 + 4H_2O(g) = Fe_3O_4 + 6HCl(g) + H_2(g)$				
		230	1.00	$Fe_3O_4 + 8HCl(g) = FeCl_2 + 2FeCl_3 + 4H_2O(g)$				
72	Calcium-Iron Bromide-2	600	0.50	$2Br_2(g) + 2CaO = 2CaBr_2 + O_2(g)$	40	40	45.77	59.23
		600	1.00	$3FeBr_2 + 4H_2O(g) = Fe_3O_4 + 6HBr(g) + H_2(g)$				
		750	1.00	$CaBr_2(l) + H_2O(g) = CaO + 2HBr(g)$				
		300	1.00	$Fe_3O_4 + 8HBr(g) = Br_2(g) + 3FeBr_2 + 4H_2O(g)$				
73	Hybrid Bismuth-Sulfur	850	1.00	$H_2SO_4(g) + Bi_2O_3(s) = Bi_2O_3SO_3(s) + H_2O$	24.23	24.23	37.69	43.46
		800	0.50	$2SO_3(g) = 2SO_2(g) + O_2(g)$				
		900	1.00	$Bi_2O_3SO_3(s) = Bi_2O_3(l) + SO_3$				
		77	1.00	$SO_2(g) + 2H_2O(l) = H_2SO_4(l) + H_2(g)$				
74	Iron Chloride-8	610	0.75	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	21.54	21.54	31.15	40.77
		420	1.50	$2FeCl_3(g) = Cl_2(g) + 2FeCl_2(s)$				
		650	1.00	$3FeCl_2(s) + 4H_2O = Fe_3O_4(s) + 6HCl + H_2(g)$				
		350	0.25	$4Fe_3O_4(s) + O_2(g) = 6Fe_2O_3(s)$				
		120	1.50	$Fe_2O_3(s) + 6HCl = 2FeCl_3(s) + 3H_2O$				

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PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
75	Magnesium-Sulfur-Iodine-1	77	1.00	2HI + H2SO4 + 2MgO(s) = MgI2(s) + MgSO4(s) + 2H2O	11.15	11.15	30.38	26.54
		300	1.00	2HI = I2(g) + H2(g)				
		1130	0.50	2MgSO4(s) = 2MgO(s) + 2SO2(g) + O2(g)				
		100	1.00	I2 + SO2(a) + 2H2O = 2HI(a) + H2SO4(a)				
		400	1.00	MgI2(a) + H2O = 2HI + MgO(s)				
76	Zinc-Selenium-Chlorine	77	1.00	2HCl + ZnSe(s) = H2Se(g) + ZnCl2(s)	9.42	9.42	24.81	28.65
		930	0.50	2ZnSO4(s) = 2SO2 + 2ZnO(s) + O2(g)				
		200	1.00	H2Se(g) = Se(s) + H2(g)				
		630	1.00	Se(l) + SO2 + 2ZnO(s) = ZnSe(s) + ZnSO4(s)				
		630	1.00	ZnCl2(l) + H2O = 2HCl + ZnO(s)				
77	Copper-Ammonium Chloride	600	1.00	2Cu + 2NH4Cl(g) = 2CuCl(l) + 2NH3 + H2(g)	22.31	22.31	35.77	41.54
		80	1.00	2CuCl(s) + 2NH3 + H2O = Cu2O(s) + 2NH4Cl(s)				
		900	0.50	4CuO(s) = 2Cu2O(s) + O2(g)				
		100	2.00	Cu2O(s) +H2SO4(l) =Cu(s) +CuSO4(s) +H2O				
		850	2.00	CuSO4(s) = CuO(s) + SO3(g)				
		300	2.00	SO3(g) + H2O = H2SO4(l)				
78	Mercury-Calcium-Bromide-4	200	1.00	2HBr(g) + Hg(l) = HgBr2 + H2(g)	18.08	18.08	23.85	35.38
		500	0.50	2HgO(l) = 2Hg(g) + O2(g)				
		200	1.00	Ca(OH)2 + HgBr2 = CaBr2 + HgO + H2O(g)				
		730	1.00	CaBr2 + 2H2O(g) = Ca(OH)2 + 2HBr(g)				
80	Uranium-Magnesium Iodide	700	0.50	6UO3(s) = 2U3O8(s) + O2(g)	17.69	17.69	21.54	33.08
		0	1.00	I2(s) + MgO(s) + U3O8(s) = MgI2(a) + 3UO3(s)				
		227	1.00	MgI2(s) +2H2O(g) = I2(g) +Mg(OH)2(s) +H2(g)				
81	Copper-Magnesium Iodide	300	1.00	2HI = I2(g) + H2(g)	10.38	10.38	29.62	27.69
		900	0.50	4CuO(s) = 2Cu2O(s) + O2(g)				
		0	1.00	Cu2O(s) + I2(s) + Mg(OH)2(s) = 2CuO(s) + MgI2(a) + H2O(l)				
		227	1.00	MgI2(s) + 2H2O(g) = 2HI(g) + Mg(OH)2(s)				
82	Manganese-Magnesium Iodide-1	300	1.00	2HI = I2(g) + H2(g)	21.92	27.69	10.38	10.38
		487	0.50	4MnO2(s) = 2Mn2O3(s) + O2(g)				
		27	1.00	I2(s) + Mg(OH)2(s) + Mn2O3(s) =MgI2(a) + 2MnO2(s) + H2O(l)				
		227	1.00	MgI2(s) + 2H2O(g) = 2HI(g) + Mg(OH)2(s)				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
83	Manganese-Magnesium Iodide-2	300	1.00	$2HI = I_2(g) + H_2(g)$	6.92	6.92	24.23	26.15
		27	0.50	$2I_2 + 2Mg(OH)_2(s) + Mn_3O_4(s) = 2MgI_2(a) + 3MnO_2(s) + 2H_2O(l)$				
		487	0.38	$4MnO_2(s) = 2Mn_2O_3(s) + O_2(g)$				
		977	0.13	$6Mn_2O_3 = 4Mn_3O_4 + O_2(g)$				
		227	1.00	$MgI_2(s) + 2H_2O(g) = 2HI(g) + Mg(OH)_2(s)$				
84	Cobalt-Magnesium Iodide	884	0.50	$2Co_3O_4(s) = 6CoO(s) + O_2(g)$	9.23	9.23	22.69	28.46
		300	1.00	$2HI = I_2(g) + H_2(g)$				
		0	1.00	$3CoO(s) + I_2(s) + Mg(OH)_2(s) = Co_3O_4(s) + MgI_2(a) + H_2O(l)$				
		227	1.00	$MgI_2(s) + 2H_2O(g) = 2HI(g) + Mg(OH)_2(s)$				
85	Arsenic-Magnesium Iodide	877	0.25	$2As_2O_5(g) = As_4O_6(g) + 2O_2(g)$	9.23	9.23	20.77	28.46
		300	1.00	$2HI = I_2(g) + H_2(g)$				
		27	0.25	$As_4O_6(s) + 4I_2(s) + 4Mg(OH)_2(s) = 2As_2O_5(s) + 4MgI_2(a) + 4H_2O(l)$				
		227	1.00	$MgI_2(s) + 2H_2O(g) = 2HI(g) + Mg(OH)_2(s)$				
86	Magnesium-Selenium Iodide	300	1.00	$2HI = I_2(g) + H_2(g)$	20.19	8.65	8.65	8.65
		27	0.50	$2SeO_3(s) = 2SeO_2(s) + O_2(g)$				
		27	1.00	$I_2(s) + Mg(OH)_2(s) + SeO_2(s) = MgI_2(a) + SeO_3(a) + H_2O(l)$				
		227	1.00	$MgI_2(s) + 2H_2O(g) = 2HI(g) + Mg(OH)_2(s)$				
87	Arsenic-Scandium Iodide	877	0.25	$2As_2O_5(l) = As_4O_6(g) + 2O_2(g)$	9.23	9.23	20.77	28.46
		300	1.00	$2HI = I_2(g) + H_2(g)$				
		227	1.33	$2ScI_3(s) + 3H_2O(l) = 6HI(g) + Sc_2O_3(s)$				
		27	0.083	$3As_4O_6(s) + 12I_2(s) + 4Sc_2O_3(s) = 6As_2O_5(s) + 8ScI_3(a)$				
88	Cobalt-Scandium Iodide	884	0.50	$2Co_3O_4(s) = 6CoO(s) + O_2(g)$	9.23	9.23	22.69	28.46
		300	1.00	$2HI = I_2(g) + H_2(g)$				
		227	0.33	$2ScI_3(s) + 3H_2O(l) = 6HI(g) + Sc_2O_3(s)$				
		27	0.33	$9CoO(s) + 3I_2(s) + Sc_2O_3(s) = 3Co_3O_4(s) + 2ScI_3(a)$				
89	Magnesium-Scandium Iodide	300	1.00	$2HI = I_2(g) + H_2(g)$	5.38	5.38	24.62	20.77
		1130	0.50	$2MgSO_4(l) = 2MgO(s) + 2SO_2(g) + O_2(g)$				
		227	0.33	$2ScI_3(s) + 3H_2O(l) = 6HI(g) + Sc_2O_3(s)$				
		27	0.33	$3I_2(s) + Sc_2O_3(s) + 3MgSO_3(s) = 2ScI_3(a) + 3MgSO_4(a)$				
		337	1.00	$MgO(s) + SO_2(g) = MgSO_3(s)$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
90	Carbon-Aluminum Bromide	27	0.17	$2Al_2O_3(s) + 6Br_2(l) = 3O_2(g) + 4AlBr_3$	31.54	31.54	50.77	48.85
		1027	0.33	$2AlBr_3(g) + 3CO_2(g) = Al_2O_3(s) + 3Br_2(g) + 3CO(g)$				
		450	1.00	$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$				
91	Carbon-Scandium Bromide	1000	0.33	$3CO_2(g) + 2ScBr_3(g) = 3Br_2(g) + 3CO(g) + Sc_2O_3(s)$	30.96	30.96	50.19	48.27
		27	0.17	$6Br_2(l) + 2Sc_2O_3(s) = 4ScBr_3(a) + 3O_2(g)$				
		450	1.00	$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$				
92	Tungsten-MagnesiumSulfate	1130	0.50	$2MgSO_4(l) = 2MgO(s) + 2SO_2(g) + O_2(g)$	21.73	21.73	40.96	37.12
		337	0.50	$MgO(s) + SO_2(g) = MgSO_3(s)$				
		127	1.00	$WO_2(s) + H_2O(g) = WO_3(s) + H_2(g)$				
		527	0.50	$WO_3(s) + MgSO_3(s) = WO_2(s) + MgSO_4(s)$				
93	Tungsten-Aluminum Bromide	27	0.17	$2Al_2O_3(s) + 6Br_2(l) = 3O_2(g) + 4AlBr_3$	24.62	26.54	28.46	38.08
		687	0.33	$2AlBr_3(g) + 3WO_3(s) = Al_2O_3 + 3Br_2(g) + 3WO_2(s)$				
		127	1.00	$WO_2(s) + H_2O(l) = WO_3(s) + H_2(g)$				
94	Tungsten-Scandium Bromide	875	0.33	$2ScBr_3(s) + 3WO_3(s) = 3Br_2(g) + Sc_2O_3(s) + 3WO_2(s)$	24.62	24.62	36.15	43.85
		27	0.17	$6Br_2(l) + 2Sc_2O_3(s) = 4ScBr_3(a) + 3O_2(g)$				
		127	1.00	$WO_2(s) + H_2O(l) = WO_3(s) + H_2(g)$				
95	Tungsten-Cerium Sulfate	407	0.50	$2Ce_2(SO_4)_3(s) + 2WO_3(s) = CeO_2(s) + 3Ce(SO_4)_2(l) + 2WO_2(s)$	16.73	16.73	26.35	35.96
		547	1.00	$2CeO_2(s) + 3SO_2(g) + O_2(g) = Ce_2(SO_4)_3(s)$				
		827	1.50	$Ce(SO_4)_2(l) = CeO_2 + 2SO_2(g) + O_2(g)$				
		127	1.00	$WO_2(s) + H_2O(l) = WO_3(s) + H_2(g)$				
96	Sodium-Magnesium Sulfate	227	1.00	$Na_2SO_3(s) + H_2O(g) = Na_2SO_4(s) + H_2(g)$	22.69	22.69	41.92	38.08
		1130	0.50	$2 MgSO_4(s) = 2 MgO(s) + 2SO_2(g) + O_2(g)$				
		337	1.00	$MgO(s) + SO_2(g) = MgSO_3(s)$				
		27	1.00	$MgSO_3(s) + Na_2SO_4(s) = MgSO_4(a) + Na_2SO_3(s)$				
97	Iron-Magnesium Sulfate	155	1.00	$2FeO(s) + H_2O(g) = Fe_2O_3(s) + H_2(g)$	21.15	21.15	40.38	36.54
		1130	0.50	$2MgSO_4(s) = 2MgO(s) + 2SO_2(g) + O_2(g)$				
		127	1.00	$2CO_2(g) + Fe_2O_3(s) + MgSO_3(s) = 2FeCO_3(s) + MgSO_4(s)$				
		177	0.67	$3FeCO_3(s) = 3CO_2(g) + 3FeO(s)$				
		337	1.00	$MgO(s) + SO_2(g) = MgSO_3(s)$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
98	Hybrid Silver	227	1.00	$2Ag + 2HCl(g) = 2AgCl + H2(g)$	19.23	19.23	36.54	38.46
		337	1.00	$2AgCl + H2SO4(l) = Ag2SO4 + 2HCl(g)$				
		967	1.00	$Ag2SO4(l) = 2Ag(l) + SO2(g) + O2(g)$				
		77	1.00	$SO2(g) + 2H2O(l) = H2SO4(l) + H2(g)$				
99	Silver Chromate	187	0.33	$4Ag + O2(g) = 2Ag2O$	28.27	28.27	47.5	45.58
		707	0.165	$4Ag2CrO4 = 8Ag + 2Cr2O3 + 5O2(g)$				
		27	0.66	$Ag2O + K2CrO4 + H2O(l) = Ag2CrO4 + 2KOH(a)$				
		1027	0.33	$Cr2O3 + 4KOH(a) + H2O(g) = 2K2CrO4(l) + 3H2(g)$				
102	Multivalent Sulfur-1	800	1.00	$H2S(g) = S(g) + H2(g)$	22.88	22.88	34.42	42.12
		850	0.50	$2H2SO4(g) = 2SO2(g) + 2H2O(g) + O2(g)$				
		700	0.50	$3S(g) + 2H2O(g) = 2H2S(g) + SO2(g)$				
		25	0.50	$3SO2(g) + 2H2O(l) = 2H2SO4(a) + S$				
		25	1.00	$S + O2(g) = SO2(g)$				
103	Cerium Chloride	450	1.00	$2CeClO + 2H2O = 2CeO2 + 2HCl + H2(g)$	26.15	26.15	35.77	45.38
		25	1.00	$2CeO2(s) + 8HCl(g) = 2CeCl3 + Cl2(g) + 4H2O$				
		610	0.50	$2Cl2(g) + 2H2O(g) = 4HCl(g) + O2(g)$				
		425	2.00	$CeCl3 + H2O = CeClO + 2HCl(g)$				
104	Magnesium-Cerium Chloride	25	1.00	$2CeCl3 + 3Mg(OH)2 = Ce2O3 + 3MgCl2(a) + 3H2O$	33.08	31.15	19.62	19.62
		25	1.00	$2CeO2 + 8HCl(g) = 2CeCl3 + Cl2(g) + 4H2O(l)$				
		25	0.50	$2Cl2(g) + 2Mg(OH)2 = 2MgCl2(a) + 2H2O(l) + O2(g)$				
		25	1.00	$Ce2O3 + H2O(l) = 2CeO2 + H2(g)$				
		450	4.00	$MgCl2(s) + 2H2O(g) = 2HCl(g) + Mg(OH)2(l)$				
105	Manganese-Ethane-Ethylene	487	0.50	$4MnO2(s) = 2Mn2O3(s) + O2(g)$	46.92	46.92	56.54	66.15
		no T	1.00	$C2H4(g) + Mn2O3 + H2O = C2H6(g) + 2MnO2(s)$				
		800	1.00	$C2H6(g) = C2H4(g) + H2(g)$				
106	High temperature electrolysis	850-2700	0.00	$2H2O = 2H2(g) + O2(g)$	74.23	74.23	93.46	91.54
107	Low Temperature Electrolysis	50	0.00	$2H2O = 2H2(g) + O2(g)$	78.85	78.85	78.85	78.85
108	Direct thermal decomposition	2200	0.00	$2H2O = 2H2(g) + O2(g)$	76.15	76.15	76.15	76.15

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
110	Sodium-Manganese-3	100	2.00	2a-NaMnO2 + H2O = Mn2O3 + 2NaOH(a)	43.27	43.27	56.73	50.96
		1560	1.00	2Mn2O3(l) = 4MnO(l) + O2(g)				
		630	2.00	2MnO(l) + 2NaOH(l) = 2a-NaMnO2 + H2(g)				
111	Sodium-Manganese Ferrite-1	1000	1.00	2MnFe2O4(s) + 3Na2CO3 + H2O = 2Na3MnFe2O6(s) + 3CO2(g) + H2(g)	44.62	44.62	63.85	61.92
		600	0.50	4Na3MnFe2O6(s) + 6CO2 = 4MnFe2O4(s) + 6Na2CO3(s) + O2(g)				
112	Iron Chloride-9	1530	0.50	2Fe3O4 +12HCl(g) = 6FeCl2 +6H2O +O2(g)	41.15	41.15	54.62	50.77
		650	1.00	3FeCl2 + 4H2O = Fe3O4 + 6HCl + H2(g)				
114	Hybrid Nitrogen-Iodine	0	2.00	2HNO3(a) + 2KI(a) = 2KNO3(a) + I2(s) + H2(g) (V=?)	13.27	13.27	17.12	28.65
		0	1.00	2NO(g) + O2(g) = 2NO2(g)				
		0	2.00	3NO2(g) + H2O = 2HNO3 + NO(g)				
		700	2.00	I2 + 2KNO3 = 2KI(l) + 2NO2(g) + O2(g)				
115	Magnesium-Sulfur-Iodine-2	300	1.00	2HI = I2(g) + H2(g)	12.69	12.69	31.92	28.08
		1130	0.50	2MgSO4(l) = 2MgO(s) + 2SO2(g) + O2(g)				
		400	1.00	MgI2(a) + H2O = 2HI + MgO				
		100	1.00	2MgO + SO2(g) + I2 = MgSO4(a) + MgI2(a)				
116	Methanol-Sulfur-Iodine	850	0.50	2H2SO4 = 2SO2 + 2H2O + O2(g)	26.15	26.15	37.69	45.38
		0	1.00	CH3I(l) + HI = CH4 + I2(s)				
		0	1.00	CH3OH(l) + HI = CH3I(l) + H2O				
		700	1.00	CH4(g) + H2O(g) = CO(g) + 3H2(g)				
		230	1.00	CO(g) + 2H2(g) = CH3OH(g)				
		100	1.00	I2(s) + SO2(a) + 2H2O = 2HI(a) + H2SO4(a)				
117	Nickel-Sulfur-Iodine-1	200	0.50	2HI +H2SO4 +2Ni(s) = NiI2(s) NiSO4(s) +2H2(g)	9.23	9.23	28.46	26.54
		800	0.50	2SO3(g) = 2SO2(g) + O2(g)				
		100	0.50	I2 + SO2(a) + 2H2O = 2HI(a) + H2SO4(a)				
		700	0.50	NiI2(s) = I2(g) + Ni(s)				
		200	0.50	NiO(s) + H2(g) = Ni(s) + H2O				
		1100	0.50	NiSO4 = NiO(s) + SO3				
118	Lanthanum Sulfate	1077	0.00	2[La2O2SO4]2[La2(SO3)(SO4)2]3 =10La2O2SO4 + 12SO2 + 3O2(g)	23.46	23.46	42.69	40.77
		500	0.00	[La2O2SO4]2[La2(SO3)2SO4*8H2O]3 + 3I2 =[La2O2SO4]2[La2(SO3)2SO4]3 + 6HI +21 H2O				
		67	0.00	5La2O2SO4 + 6SO2 + 24H2O = [La2O2SO4]2[La2(SO3)2SO4*8H2O]3				
		300	0.00	2HI = I2(g) + H2(g)				

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PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
119	Nitrogen-Iodine-2	700	0.50	$2I_2(g) + 2Na_2CO_3(s) = 2CO_2(g) + 4NaI(l) + O_2(g)$	9.62	9.62	13.46	25
		127	1.00	$2NaHCO_3(s) = CO_2(g) + Na_2CO_3(s) + H_2O(g)$				
		500	1.00	$2NH_4I(s) = I_2(g) + 2NH_3 + H_2(g)$				
		100	2.00	$CO_2 + NaI(s) + NH_3 + H_2O = NaHCO_3(s) + NH_4I(s)$				
120	Promethium Sulfate	1077	0.00	$2[Pr_2O_2SO_4]2[Pr_2(SO_3)(SO_4)_2]3 = 10Pr_2O_2SO_4 + 12SO_2 + 3O_2$	11.92	11.92	31.15	29.23
		500	0.00	$[Pr_2O_2SO_4]2[Pr_2(SO_3)2SO_4*4H_2O]3 + 3I_2 = [Pr_2O_2SO_4]2[Pr_2(SO_3)(SO_4)_2]3 + 6HI + 9H_2O$				
		300	0.00	$2HI = I_2(g) + H_2(g)$				
		67	0.00	$5Pr_2O_2SO_4 + 6SO_2 + 12H_2O = [Pr_2O_2SO_4]2[Pr_2(SO_3)2SO_4*4H_2O]3$				
121	Multivalent Sulfur-2	700	0.50	$3S + 2H_2O(g) = 2H_2S(g) + SO_2(g)$	34.81	34.81	46.35	54.04
		0	0.50	$3SO_2(g) + 2H_2O(l) = 2H_2SO_4(a) + S(s)$				
		850	0.50	$2H_2SO_4(g) = 2SO_2(g) + 2H_2O(g) + O_2(g)$				
		800	0.50	$2H_2S(g) = S_2(g) + 2H_2(g)$				
124	Copper Sulfate-1	300	0.33	$2Cu_2O(s) + 4SO_2 + 3O_2 = 4CuSO_4(l)$	34.42	44.04	24.81	26.73
		500	0.17	$2Cu_2O(s) + 8CuSO_4(l) = 12Cu(s) + 8SO_2 + 9O_2$				
		500	1.00	$2Cu(s) + H_2O(g) = Cu_2O(s) + H_2$				
126	Cesium Amalgum-2	600	0.50	$2HgO = 2Hg + O_2$	12.88	24.42	10.96	18.65
		0	1.00	$2CsHg_y + 2H_2O = 2CsOH + 2Hg + H_2$				
		410	0.50	$4CsOH + (x+1)O_2 = 4CsO_x + 2H_2O$ (let $x=2, y=1$)				
		300	2.00	$CsO_x + (x+y)Hg = CsHg_y + xHgO$				
127	Vanadium Oxychloride-2	600	1.00	$4VOCl_2(l) = 2VOCl(s) + 2VOCl_3(g)$	29.04	29.04	40.58	48.27
		170	1.00	$2HCl + 2VOCl(s) = 2VOCl_2(s) + H_2$				
		850	0.50	$2Cl_2 + 2H_2O = 4HCl + O_2$				
		200	1.00	$2VOCl_3(g) = Cl_2 + 2VOCl_2(s)$				
129	Magnesium Sulfate	995	0.50	$2MgSO_4(s) = 2MgO(s) + 2SO_2 + O_2$	45.38	45.38	62.69	64.62
		0	1.00	$MgO(s) + SO_2 + H_2O(l) = MgSO_4(s) + H_2$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
130	Magnesium-Carbon Disulfide	995	0.333	2MgSO4 = 2MgO + 2SO2 + O2	28.65	28.65	47.88	44.04
		0	0.333	2 MgSO4(s) + H2S = 2 MgO(s) + 3 SO2 + H2				
		0	0.667	MgO(s) +S(s) +SO2 +H2O = MgSO4(s) +H2S				
		0	0.083	3CS2 + 4 H2O = 3 C + 4 H2S + 2 SO2				
		850	0.333	2H2S(g) = S2(g) + 2H2				
		0	0.083	3 C + 8 MgO(s) + 14 SO2 = 3 CS2 + 8 MgSO4(s) + 2 O2				
131	Manganese Sulfate	1100	0.50	2MnSO4(s) = 2MnO(s) + 2SO2 + O2	45	45	64.23	62.31
		290	1.00	MnO(s) + SO2 + H2O = MnSO4(s) + H2				
132	Ferrous Sulfate-3	1100	0.50	2FeSO4(s) = 2FeO(s) + 2SO2 + O2	44.23	44.23	63.46	61.54
		236	1.00	FeO(s) + SO2 + H2O = FeSO4(s) + H2				
133	Ferrous Sulfate-4	0	0.50	2Fe3O4(s) + 6 SO3 = 6 FeSO4(s) + O2	35.58	35.58	54.81	52.88
		550	1.00	FeO(s) + H2O = Fe3O4(s) + H2				
		1100	3.00	FeSO4(s) = FeO(s) + SO3(g)				
134	Cobalt Sulfate	1100	0.50	2CoSO4(l) =2CoO(s) + 2SO2 + O2	41.15	41.15	60.38	58.46
		190	1.00	CoO(s) + H2O + SO2 = CoSO4(s) + H2				
135	Copper Sulfate-2	0	1.00	Cu2O(s) + H2O(l) = Cu(s) + Cu(OH)2(s)	23.27	23.27	32.88	42.5
		45	1.00	Cu(OH)2(s) + SO2 = CuSO4(s) + H2				
		800	0.50	2Cu(s) +2CuSO4(s) =2Cu2O(s) +2SO2 + O2				
136	Copper Sulfate-3	0	1.00	CuO(s) + SO2 + 6 H2O(l) = CuSO4(5 H2O)(s) + H2	25.96	25.96	41.35	45.19
		850	0.50	2 CuSO4(s) = 2 CuO(s) + 2 SO3(g)				
		150	1.00	CuSO4(5 H20)(s) = CuSO4(s) + 5 H2O				
		950	0.50	2SO3(g) = 2SO2 + O2				
137	Zinc-Barium Sulfate	0	0.50	3SO2 + 2ZnO(s) = S(s) + 2ZnSO4(s)	30.58	30.58	49.81	47.88
		930	0.50	2ZnSO4(s) = 2SO2 + 2ZnO(s) + O2				
		870	0.25	BaS(s) + 4H2O = BaSO4(s) + 4H2				
		1020	0.25	BaSO4(s) + 2S(g) = BaS(s) +2 SO2				
138	Copper-Iron Chloride	800	0.50	2Cl2 + 2H2O = 4 HCl + O2	8.27	8.27	17.88	27.5
		550	1.00	2CuCl2(s) = 2CuCl(l) + Cl2				
		650	1.00	3FeCl2(s) + 4H2O = Fe3O4(s) + 6HCl + H2				
		110	1.00	Fe3O4(s) + 8HCl(a) = FeCl2(a) +2FeCl3(a) + 4H2O				
		100	1.00	2CuCl(s) + 2FeCl3(a) = 2CuCl2(a) + 2FeCl2(a)				

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PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
139	Calcium-Iron Bromide-1	760	1.00	$CaBr_2(l) + H_2O = CaO(s) + 2HBr$	28.08	28.08	35.77	47.31
		200	1.00	$2FeBr_3(s) = Br_2 + 2FeBr_2(s)$				
		500	0.50	$2Br_2 + 2CaO(s) = 2CaBr_2(s) + O_2$				
		650	1.00	$3FeBr_2(s) + 4H_2O = Fe_3O_4(s) + 6HBr + H_2$				
		120	1.00	$Fe_3O_4(s) + 8HBr(a) = FeBr_2(a) + 2FeBr_3(a) + 4H_2O$				
140	Iron Chloride-10	400	1.00	$3FeO(s) + H_2O(g) = Fe_3O_4(s) + H_2$	25	25	44.23	42.31
		1030	0.50	$2Cl_2 + 2H_2O = 4HCl + O_2$				
		380	1.00	$Fe_3O_4(s) + 8HCl(g) = 3FeCl_2(s) + 4H_2O(g) + Cl_2$				
		690	1.00	$3FeCl_2(l) + 3H_2O (+H_2) = 3FeO(s) + 6 HCl$				
141	Iron-Sulfur-Iodine	900	0.25	$4CO_2 + 3FeI_2(g) = 4CO + Fe_3O_4(s) + 3I_2(g)$	16.92	16.92	30.38	36.15
		200	0.25	$Fe_3O_4(s) + 8HI(g) = 3FeI_2(s) + 4H_2O + I_2(l)$				
		400	0.50	$2CO + 2H_2O = 2CO_2 + 2H_2$				
		40	1.00	$I_2(s) + SO_2(a) + 2H_2O = 2HI(a) + H_2SO_4(a)$				
		850	0.50	$2H_2SO_4(g) = 2SO_2 + 2H_2O + O_2$				
142	Sulfur-Methanol	230	1.00	$CO + 2H_2 = CH_3OH(g)$	32.88	32.88	44.42	52.12
		830	1.00	$CH_4 + H_2O = CO + 3H_2$				
		850	0.50	$2H_2SO_4(g) = 2SO_2 + 2H_2O + O_2$				
		100	1.00	$CH_3OH(g) + SO_2 + H_2O = CH_4 + H_2SO_4(l)$				
143	Nickel-Sulfur-Iodine-2	400	1.00	$NiO(s) + H_2 = Ni(s) + H_2O$	9.23	9.23	20.77	28.46
		600	1.00	$NiI_2(s) = I_2(g) + Ni(s)$				
		850	0.50	$2NiSO_4(s) = 2NiO(s) + 2SO_2 + O_2$				
		40	1.00	$I_2(s) + SO_2(a) + 2H_2O = 2HI(a) + H_2SO_4(a)$				
		50	1.00	$2HI(a) + H_2SO_4(a) + 2 Ni(s) = NiI_2(a) + NiSO_4(a) + 2H_2$				
144	Barium-Iron-Sulfur	870	0.25	$BaS(s) + 4H_2O = BaSO_4(s) + 4H_2$	31.35	31.35	50.58	48.65
		930	0.50	$4FeSO_4(s) = 2Fe_2O_3(s) + 4SO_2 + O_2$				
		430	0.50	$2Fe_2O_3(s) + 5SO_2 = 4FeSO_4(s) + S(l)$				
		1020	0.25	$BaSO_4(s) + 2S(g) = BaS(s) + 2 SO_2$				
145	Nickel-Ammonium Iodide	700	0.50	$2I_2(g) + 2Na_2CO_3(s) = 2CO_2 + 2NaI(l) + O_2$	19.23	19.23	28.85	38.46
		300	1.00	$2NaHCO_3(s) = CO_2 + Na_2CO_3(s) + H_2O$				
		60	1.00	$2CO_2 + 2NH_3(a) + 2NaI(a) + 2H_2O = 2NaHCO_3(a) + 2NH_4I(a)$				
		500	1.00	$2NH_4I(s) + Ni(s) = 2NH_3 + NiI_2(s) + H_2$				
		800	1.00	$NiI_2(l) = I_2(g) + Ni(s)$				
146	Hybrid Antimony-Iodine	5	0.50	$Sb_2O_3 + 2H_2O + 2I_2 = 4HI(a) + Sb_2O_5$	19.04	19.04	38.27	36.35
		80	1.00	$2HI(a) = I_2 + H_2$				
		1000	0.50	$Sb_2O_5(s) = Sb_2O_3(l) + O_2$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
147	Cadmium Sulfate	200	1.00	$CdO + SO_2 + H_2O = CdSO_4 + H_2$	37.88	37.88	57.12	55.19
		1000	0.50	$2CdSO_4 = 2CdO + 2SO_2 + O_2$				
148	Ferrous Sulfate-5	725	1.00	$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$	32.5	32.5	47.88	51.73
		125	1.00	$Fe_2O_3 + 2SO_2 + H_2O = 2FeSO_4 + H_2$				
		950	0.50	$2SO_3 = 2SO_2 + O_2$				
149	Barium-Molybdneum Sulfate	25	1.00	$BaMoO_4 + SO_2 + H_2O = BaSO_3 + MoO_3 + H_2O$	39.04	39.04	58.27	56.35
		1000	0.50	$2BaSO_4 + 2MoO_3 = 2BaMoO_4 + 2SO_2 + O_2$				
		25	1.00	$BaSO_3 + H_2O = BaSO_4 + H_2$				
150	Germanium-Cobalt	400	1.00	$3CoO(s) + SO_3(g) = Co_3O_4(s) + SO_2$	24.23	24.23	43.46	41.54
		900	1.00	$Ge(s) + H_2O(g) = GeO(s) + H_2$				
		800	1.00	$GeO(s) + SO_2 = Ge(s) + SO_3(g)$				
		1000	0.50	$2Co_3O_4(s) = 6CoO(s) + O_2$				
151	Carbon-Sulfur	950	0.50	$2 H_2SO_4(g) = 2SO_2(g) + 2H_2O + O_2$	37.5	37.5	52.88	56.73
		500	1.00	$CO + H_2O = CO_2 + H_2$				
		350	1.00	$CO_2 + SO_2(g) + H_2O = CO + H_2SO_4(l)$				
152	Iron-Zinc	600	0.25	$2Fe_3O_4(s) + 3Zn(l) + 4H_2O = 3ZnFe_2O_4(s) + 4H_2$	49.04	49.04	66.35	62.5
		>1300	0.25	$3ZnFe_2O_4(s) = 2Fe_3O_4(s) + 3Zn(g) + 2O_2$				
153	Sodium-Manganese Ferrite-2	800	1.00	$2MnFe_2O_4 + 3Na_2CO_3 + H_2O = 3CO_2 + 2Na_3MnFe_2O_6 + H_2$	28.08	28.08	47.31	45.38
		1000	0.50	$6Fe_2O_3(s) + 4Na_3MnFe_2O_6 = 4MnFe_2O_4 + 12NaFeO_2(s) + O_2$				
		600	3.00	$CO_2 + 2NaFeO_2 = Fe_2O_3 + Na_2CO_3$				
154	Sodium Ferrite	800	1.00	$CO_2 + 2Na_2FeO_2 + H_2O = Na_2CO_3 + 2NaFeO_2 + H_2$	46.35	46.35	52.12	46.35
		2000	0.50	$2Na_2CO_3 + 4NaFeO_2 = 2CO_2 + 4Na_2FeO_2 + O_2$				
155	Iodine-Mercury	100	2.00	$CO_2 + KI(aq) + NH_3 + H_2O = KHCO_3(s) + NH_4I(aq)$ (in aqueous alcohol, up to 7 atm)	8.46	18.08	8.46	18.08
		200	1.00	$2KHCO_3(s) = CO_2 + K_2CO_3(s) + H_2O$				
		427	1.00	$Hg(g) + 2NH_4I(s) = HgI_2(g) + 2NH_3 + H_2$				
		627	0.50	$2HgI_2(g) + 2K_2CO_3(s) = 2CO_2 + 2Hg(g) + 4KI(s) + O_2$				
156	Potassium Chromate	900	0.50	$Cr_2O_3 + 6KOH(l) = 2K_3CrO_4(s) + 2H_2 + H_2O$	20.96	20.96	34.42	40.19
		100	0.50	$6K_3CrO_4(aq) + 5H_2O = Cr_2O_3(s) + 4K_2CrO_4(aq) + 10KOH(aq)$				
		700	0.50	$4K_2CrO_4(s) + 4KOH(l) = 4K_3CrO_4(s) + 2H_2O + O_2$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
157	Strontium Chromate	740	1.00	Cr2O3(s)+4SrO(s)+H2O(g) =2Sr2CrO4(s) +H2	18.46	18.46	24.23	35.77
		580	0.67	3SrCrO4(s) + 2Sr(OH)2(l) = Sr5(CrO4)3OH(s) + 3/2H2O + 3/4O2				
		100	0.33	6Sr2CrO4(aq) + 2 Sr5(CrO4)3OH(aq) + 15H2O = 3Cr2O3(s) + 6SrCrO4(aq) + 16Sr(OH)2(aq)				
		700	4.00	Sr(OH)2(l) = SrO(s) + H2O(g)				
158	Barium Chromate	700	1.00	4Ba(OH)2(l) + Cr2O3(s) = 2Ba2CrO4(s) + 3H2O + H2	33.65	33.65	49.04	52.88
		100	1.00	2Ba2CrO4(s) + Ba3(CrO4)2(s) + 5H2O = 2BaCrO4(aq) + 5Ba(OH)2(aq) + Cr2O3(s)				
		950	0.50	4BaCrO4(s) + 2Ba(OH)2(l) = 2Ba3(CrO4)2(s) + 2H2O + O2				
159	Sulfur-Ethane-Ethylene	350	1.00	C2H4 + SO2 + 2H2O = C2H6 + H2SO4	39.23	39.23	50.77	58.46
		800	1.00	C2H6 = C2H4 + H2				
		850	0.50	2H2SO4 = 2H2O + 2SO2 + O2				
160	Arsenic-Iodine	40	0.50	As2O3 + 2I2 + 5H2O = 2H3AsO4(s) + 4HI(g) (in diethylether, CS2)	25.38	33.08	27.31	36.92
		300	0.50	2H3AsO4(s) = As2O5(s) + 3H2O				
		650	0.50	As2O5(s) = As2O3(g) + O2				
		630	1.00	2HI = H2 + I2				
161	Arsenic-Iodine-Nickel	150	0.50	As2O3 + 2I2 + 6NH3 +5H2O = 2NH4H2AsO4 + 4NH4I (in ethanol)	17.31	17.31	30.77	36.54
		300	0.50	2NH4H2AsO4 = As2O5(s) + 2NH3 + 3H2O				
		650	0.50	As2O5(s) = As2O3(g) + O2				
		550	0.50	4NH4I(g) + 2Ni = 4NH3 + 2NiI2(s) + 2H2				
		880	0.50	2NiI2(l) = 2I2(g) + 2Ni(s)				
162	Uranium Carbonate-2	300	1.00	CO + H2O = CO2 + H2	33.27	44.81	31.35	39.04
		150	1.00	4 CO2 + U3O8(s) = CO + 3UO2CO3				
		600	0.25	3UO2CO3 = 3CO2 + 3UO3				
		600	0.50	6UO3 = 2U3O8 + O2				
163	Manganese Carbonate	300	1.00	CO + H2O = CO2 + H2	37.5	49.04	35.58	43.27
		100	0.50	6CO2 + 2Mn3O4(s) = 6MnCO3 + O2				
		600	1.00	3MnCO3 = CO + 2CO2 + Mn3O4(s)				
164	Zinc-Methanol	700	1.00	CH4 + H2O = CO + 3H2	24.81	24.81	30.58	42.12
		227	1.00	CO + 2H2 = CH3OH				
		327	1.00	CH3OH +SO2 +ZnO(s) = CH4 + ZnSO4(s)				
		727	0.50	2ZnSO4(s) = 2SO2 + 2ZnO(s) + O2				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
165	Zinc-Selenium	500	1.00	$Se + SO_2 + 2ZnO = ZnSe + ZnSO_4$	20	20	25.77	39.23
		25	1.00	$H_2SO_4 + ZnSe = H_2Se + ZnSO_4$				
		750	0.50	$4ZnSO_4 = 2SO_2 + 2SO_3 + 4ZnO + O_2$				
		164	1.00	$H_2Se = Se + H_2$				
		0	1.00	$H_2O + SO_3 = H_2SO_4$				
166	Cadmium-Gallium	400	1.00	$Cd(l) + H_2O = CdO(s) +$ **H_2**	19.42	19.42	29.04	38.65
		25	0.20	$6CdO(s) + 6I_2(l) = 5CdI_2$ (in ether) $+ Cd(IO_3)_2(s)$				
		300	0.10	$2Cd(IO_3)_2 = 2CdO(s) + 2I_2(g) + 5 O_2$				
		790	1.00	$CdI_2(g) + Pb(l) = Cd(g) + PbI_2(l)$				
		600	0.33	$2Ga(l) + 3 PbI_2(l) = 2GaI_3(g) + 3Pb(l)$				
		800	0.33	$2GaI_3(g) = 2Ga(l) + 3I_2(g)$				
167	Hybrid Copper Sulfate	25	1.00	$SO_2 + 2H_2O = H_2SO_4 + H_2$ (V=)	23.65	23.65	42.88	40.96
		25	1.00	$CuO + H_2SO_4 + 4H_2O = CuSO_4.5H_2O$				
		300	1.00	$CuSO_4.5H_2O = CuSO_4(s) + 5H_2O$				
		850	1.00	$CuSO_4 = CuO + SO_3(g)$				
		850	1.00	$Cu_2O + SO_3(g) = 2CuO + SO_2$				
		1000	0.50	$4CuO(s) = 2Cu_2O(s) + O_2$				
168	Manganese Chloride-2	500	4.00	$MnCl_2(s) + H_2O = 2HCl + MnO(s)$	23.08	23.08	36.54	42.31
		900	1.00	$3MnO((s) + H_2O = Mn_3O_4(s) + H_2$				
		100	1.00	$8HCl + Mn_3O_4(s) = Cl_2 + 3MnCl_2(aq) + 4H_2O$ (aqueous slurry)				
		50	1.00	$Cl_2 + MnO(s) + Mn_2O_3(s) = MnCl_2(aq) + 2MnO_2(s)$ (aqueous slurry)				
		600	0.50	$4MnO_2(s) = 2Mn_2O_3(s) + O_2$				
169	Magnesium Iodate	150	0.20	$6I_2(l) + 6MgO(s) = 5MgI_2(s) + Mg(IO_3)_2$	21.92	21.92	25.77	37.31
		700	0.10	$2 Mg(IO_3)_2 = 2I_2(g) + 2MgO(s) + 5O_2$				
		400	0.20	$5MgI_2(s) + 5H_2O = 10 HI + 5MgO(s)$				
		300	1.00	$2HI = I_2(g) + H_2$				
170	Iron Sulfide	327	1.00	$2FeS + 4SO_2 = 2FeSO_4 + 2S_2(g)$	33.65	33.65	52.88	50.96
		827	0.50	$4FeSO_4 = 2Fe_2O_3 + 4SO_2 + O_2$				
		227	1.00	$Fe_2O_3 + 3H_2S = 2FeS + S + 3H_2O$				
		527	1.00	$3S_2(g) + 4H_2O = 4H_2S + 2SO_2$				
		1027	0.50	$2H_2S = S_2(g) + 2H_2$				
171	Hybrid Zinc-Bromine	900	0.50	$2Br_2(g) + 2ZnO(s) = 2ZnBr_2(g) + O_2$	29.04	29.04	42.5	48.27
		900	1.00	$ZnBr_2(g) + H_2O = 2HBr + ZnO(s)$				
		100	1.00	$2HBr = Br_2 + H_2$ (V=??)				
172	Hybrid Indium-Bromine	900	0.17	$6Br_2(g) + 2In_2O_3(s) = 4InBr_3(g) + 3O_2$	26.73	26.73	40.19	45.96
		900	0.33	$2InBr_3(g) + 3H_2O = 6HBr + In_2O_3(s)$				
		100	1.00	$2HBr = Br_2 + H_2$ (V=??)				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
173	Hybrid Nickel Bromide	900	0.50	$2Br_2(g) + 2NiO(s) = 2NiBr_2(s) + O_2$	29.04	29.04	42.5	48.27
		900	1.00	$NiBr_2(s) + H_2O = 2HBr + NiO(s)$				
		100	1.00	$2HBr = Br_2 + H_2$ (V=??)				
174	Hybrid Cobalt-Bromide-1	900	0.50	$2Br_2(g) + 2CoO(s) = 2CoBr_2(l) + O_2$	25.58	25.58	39.04	44.81
		900	1.00	$CoBr_2(l) + H_2O = 2HBr + CoO(s)$				
		100	1.00	$2HBr = Br_2 + H_2$ (V=??)				
175	Hybrid Manganese Bromide	900	0.50	$2Br_2(g) + 2MnO(s) = 2MnBr_2(l) + O_2$	26.15	26.15	39.62	45.38
		900	1.00	$MnBr_2(l) + H_2O = 2HBr + MnO(s)$				
		100	1.00	$2HBr = Br_2 + H_2$ (V=??)				
177	Lead Chloride	400	3.00	$2HCl + PbO = PbCl_2(s) + H_2O$	36.35	47.88	34.42	42.12
		500	1.00	$3PbCl_2(s) + 4H_2O = 6HCl + Pb_3O_4 + H_2$				
		600	0.50	$2Pb_3O_4 = 6PbO + O_2$				
179	Sodium Carbonate-Iodate-1	80	0.33	$3I_2(s) + 6Na_2CO_3(aq) + 3H_2O = 6NaHCO_3(aq) + 5NaI(aq) + NaIO_3(aq)$	19.23	19.23	23.08	34.62
		270	0.33	$6NaHCO_3(s) = 3CO_2 + 3Na_2CO_3(s) + 3H_2O$				
		450	0.33	$2NaIO_3(s) = 2NaI(s) + 3O_2$				
		25	0.33	$3 CO_2 + 6NaI(aq) + 6NH_3 + 3H_2O = 3Na_2CO_3(aq) + 6NH_4I(aq)$				
		370	0.33	$6NH_4I + 3Ni(s) = 3NiI_2(s) + 6NH_3 + 3H_2$				
		700	1.00	$NiI_2(s) = Ni(s) + I_2(g)$				
181	Nitrate-Sulfate	700	1.00	$I_2(g) + 2KNO_3 = 2KI + 2NO(g) + 2O_2$	30.38	30.38	34.23	45.77
		300	2.00	$KHSO_4 + KI = HI(g) + K_2SO_4$				
		300	1.00	$2HI = H_2 + I_2$				
		25	2.00	$HNO_3(aq) + K_2SO_4(aq) = KHSO_4(aq) + KNO_3(aq)$				
		100	1.00	$3NO_2(g) + H_2O = 2HNO_3 + NO(g)$				
		100	1.50	$2NO(g) + O_2 = 2NO_2(g)$				
182	Cadmium Carbonate	1200	0.50	$2CdO = 2Cd(g) + O_2$	34.42	34.42	53.65	49.81
		300	0.50	$2CdCO_3 = 2CO_2 + 2CdO$				
		25	1.00	$Cd + CO_2 + H_2O = CdCO_3 + H_2$				
183	Calcium-Antimony	100	0.33	$3I_2(g) + 4Sb_2O_3(s) = 2SbI_3 + 3Sb_2O_4(s)$	10.19	10.19	29.42	25.58
		100	0.33	$3CaO(s) + 2SbI_3(s) = 3CaI_2(s) + Sb_2O_3(s)$				
		1000	1.00	$CaI_2(l) + H_2O = CaO(s) + 2HI(g)$				
		300	1.00	$2HI(g) = I_2(g) + H_2(g)$				
		1130	0.50	$2Sb_2O_4(s) = 2Sb_2O_3(l) + O_2$				
184	Hybrid Antimony-Bromine	80	0.50	$2Br_2(l) + Sb_2O_3(s) + 2H_2O(l) = 4HBr(aq) + Sb_2O_5(s)$	31.35	31.35	50.58	48.65
		100	1.00	$2HBr(aq) = Br_2(l) + H_2(g)$ (V=)				
		1000	0.50	$Sb_2O_5(s) = Sb_2O_3(s) + O_2(g)$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
185	Hybrid Cobalt Bromide-2	500	1.00	$Br_2(g) + 4CoO(s) = CoBr_2(s) + Co_3O_4(s)$	28.65	28.65	42.12	47.88
		750	1.00	$CoBr_2(l) + H_2O = CoO(s) + 2HBr(g)$				
		900	0.50	$2Co_3O_4(s) = 6 CoO(s) + O_2$				
		25	1.00	$2HBr(aq) = Br_2(l) + H_2$ (V=)				
186	Hybrid Silver Sulfate	25	1.00	$2Ag + H_2SO_4 = Ag_2SO_4(aq) + H_2$ (V=)	20.58	20.58	35.96	39.81
		930	0.50	$2Ag_2SO_4(l) = 4Ag(s) + 2SO_3 + O_2$				
		300	1.00	$SO_3(g) + H_2O(g) = H_2SO_4(g)$				
188	Hybrid Ammonium Persulfate	257	1.00	$NH_3(g) + SO_2 + 2H_2O = NH_4HSO_4(aq) + H_2$ (V=)	36.15	36.15	51.54	55.38
		257	1.00	$NH_4HSO_4(aq) + Na_2SO_4(aq) = NH_3(g) + Na_2S_2O_7(aq) + H_2O$				
		927	0.50	$2Na_2S_2O_7(l) = 2Na_2SO_4(l) + 2SO_2 + O_2$				
189	Hybrid Arsenic-Bromine	25	1.00	$4HBr = 2Br_2 + 2H_2$ (V=)	21.35	21.35	27.12	40.58
		25	0.17	$5As_2O_3 + 6Br_2(g) + 9H_2O(g) = 4AsBr_3 + 6H_3AsO_4(a)$ (aqueous soln)				
		25	0.17	$4AsBr_3 + 6H_2O = 2As_2O_3 + 12HBr$ (aqueous solution)				
		750	0.17	$6H_3AsO_4 = 3As_2O_3 + 9H_2O + 3O_2$				
191	Hybrid Copper Chloride	430	1.00	$2 Cu(s) + 2 HCl(g) = 2 CuCl(l) + H_2$	45.19	56.73	39.42	43.27
		75	1.00	$4 CuCl(aq) = 2 Cu + 2 CuCl_2(aq)$ (V=)				
		550	0.50	$4CuCl_2(s) + 2H_2O = 4CuCl(l) + 4 HCl + O_2$				
192	Photocat Ammonia-Sulfur	80	1.00	$(NH_4)_2SO_3(a) + H_2O = (NH_4)_2SO_4(a) + H_2(g)$	29.42	29.42	40.96	48.65
		350	1.00	$(NH_4)_2SO_4(a) = H_2SO_4(l) + 2NH_3(g)$				
		850	0.50	$2H_2SO_4(g) = 2SO_2(g) + 2H_2O(g) + O_2(g)$				
		25	1.00	$2NH_3(g) + SO_2(g) + H_2O = (NH_4)_2SO_3(a)$				
193	Multivalent Sulfur-3	850	0.50	$2H_2SO_4(g) = 2SO_2(g) + 2H_2O(g) + O_2(g)$	34.04	34.04	47.5	41.73
		1570	0.50	$2H_2S(g) = S_2(g) + 2H_2(g)$				
		490	0.25	$3S_2(g) + 4H_2O(g) = 4H_2S(g) + 2SO_2(g)$				
		150	0.50	$3SO_2(g) + 2H_2O(l) = 2H_2SO_4(l) + S$				
194	Zinc-Manganese Ferrite	1000	1.00	$MnFe_2O_4(s) + 3 ZnO(s) + H_2O(g) = Zn_3MnFe_2O_4(s) + H_2$	51.15	51.15	70.38	66.54
		1200	0.50	$2Zn_3MnFe_2O_4(s) = 2MnFe_2O_4(s) + 6ZnO(s) + O_2$				
195	Graphite-Aluminum Chloride	300	1.00	$24C(s) + 2AlCl_3(g) + 2HCl = 2C_{12}AlCl_4(s) + H_2$	30.19	30.19	39.81	49.42
		800	1.00	$2C_{12}AlCl_4(s) = 24 C(s) + 2AlCl_3(g) + Cl_2(g)$				
		600	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$				

PID#	name	T (C)	Multiplier	Reactions	trough	tower	dish	adv tower
196	Sodium Carbonate-Iodate-2	80	0.33	$3I_2(s) + 6Na_2CO_3(aq) + 3H_2O = 6NaHCO_3(aq) + 5NaI(aq) + NaIO_3(aq)$	28.85	38.46	19.23	21.15
		127	0.33	$6NaHCO_3(s) = 3CO_2 + 3Na_2CO_3(s) + 3H_2O$				
		430	0.33	$2NaIO_3(s) = 2NaI(s) + 3O_2$				
		100	0.33	$3 CO_2 + 6NaI(aq) + 6NH_3 + 3H_2O = 3Na_2CO_3(aq) + 6NH_4I(aq)$				
		500	0.33	$6NH_4I = 3I_2(g) + 6NH_3 + 3H_2$				
198	Calcium Bromide	727	1.00	$CaBr_2(s) + H_2O(g) = CaO(s) + 2 HBr(g)$	30.58	30.58	36.35	47.88
		600	0.50	$2Br_2(g) + 2CaO(s) = 2CaBr_2(s) + O_2$				
		25	1.00	$2 HBr(g) + plasma = Br_2(g) + H_2$				
199	Iron Chloride-11	650	1.00	$6 FeCl_2 + 8 H_2O = 2 Fe_3O_4 + 12 HCl + 2H_2$	25.77	25.77	35.38	45.00
		230	0.33	$3 Fe_3O_4 + 3/2 Cl_2 = 4 Fe_2O_3 + FeCl_3$				
		230	0.33	$4 Fe_2O_3 + 24 HCl = 8 FeCl_3 + 12 H_2O$				
		430	0.33	$9 FeCl_3 = 9 FeCl_2 + 9/2 Cl_2$				
		800	0.50	$2 H_2O + 2Cl_2 = 4 HCl + O_2$				
200	Iron Chloride-12	650	1.00	$3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl(g) + H_2$	30.77	30.77	40.38	50.00
		230	1.00	$Fe_3O_4 + 8HCl = FeCl_2 + 2 FeCl_3 + 4H_2O$				
		350	1.00	$2FeCl_3 = Fe_2Cl_6 = 2 FeCl_2 + Cl_2(g)$				
		800	0.50	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2$				
201	Carbon Oxides	150	1.00	$CO + H_2O = CO_2 + H_2$	55.38	55.38	55.38	55.38
		2700	0.50	$2CO_2 = 2CO + O_2$				
202	Methanol-Formaldehyde	850	1.00	$CH_4(g) + H_2O(g) = CO(g) + H_2(g)$	43.46	43.46	55.00	62.69
		250	1.00	$CO(g) +2 H_2(g) = CH_3OH$				
		650	1.00	$CH_3OH = CH_2O(g) + H_2(g)$				
		100	0.50	$2CH_2O(g) + 2H_2 = 2CH_4 + O_2$				

APPENDIX 2

Efficiency analysis for the 63 cycles listed in Table 2 of the report.

PID 1 – SULFUR-IODINE

This process is based on the following chemical reactions:

Reaction Code	Formula	Multiplier	Proposed Temp. ($^{\circ}$C)
I2-1	$I2 + SO2(a) + 2H20 = 2HI(a) + H2SO4(A)$	1	100
H2SO4	$2H2SO4 = 2SO2 + 2H20 + O2(g)$	0.5	850
HI-1	$2HI = I2(g) + H2(g)$	1	300

This process has been studied extensively, and is under active development using a nuclear heat source. Examples of thermal efficiency are 42% (1) to 47% (2).

This is a technically feasible cycle. Costing of a solar energy flowsheet would be the next logical step.

REFERENCES

[1]   L.C. Brown, G.E. Besenbruch, R.D. Lentsch, K.R. Schultz, J.F. Funk, P.S. Pickard, A.C. Marshall, and S.K. Showalter, "High Efficiency Generation of Hydrogen Fuels using Nuclear Power, Final technical report for the period August 1, 1999 through September 30, 2002," General Atomics Report GA-A24285, June 2003.

[2]   J.H. Norman, G.E. Besenbruch, D.R. O'Keefe and C.L. Allen, "Thermochemical Water-Splitting Cycle, Bench-Scale Investigations, and Process Engineering, Final Report for the Period February 1977 through December 31, 1981," General Atomics Report GA-A16713, DOE Report DOE/ET/26225-1.

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PID 2 –NICKEL-MANGANESE FERRITE

The NiFeMn Ferrite cycle is based on the following two reactions from Ref. [1]. This PID is assumed to be representative of a large number of possible ferrite cycles. For this analysis a large number of mixed metal iron oxide systems were, therefore, evaluated. This cycle is related to PID 7, 152, and194.

Reaction Code	Formula	Multiplier	Proposed Temp. (ºC)
NiMnFe4O6	NiMnFe4O6 + 2H2O = NiMnFe4O8 + 2H2(g)	0.5	800
NiMnFe4O8	NiMnFe4O8 = NiMnFe4O6 + O2(g)	0.5	1000

For Fe_3O_4 dissociation to FeO calculations using HSC, Ref. [2], indicate a positive delta G even at temperatures as high as 3000K. Data from JANAF Thermochemical Tables, Ref. [3], indicate negative delta G at temperatures substantially less than 3000 K and the Facility for the Analysis of Chemical Thermodynamics (FACT) Ref. [4] indicates a negative delta G at a temperature 365 K less than HSC. These discrepancies are indicative of the uncertainty of thermodynamic data for metal oxides. In addition, the HSC database does not include many of the chemical compounds cited for the cycles; only includes pure phases; and does not account for solid solutions, which could lower the oxygen releasing reaction temperature. HSC, however, does indicate that mixed metal oxides of iron with manganese, magnesium or cobalt can reduce the dissociation temperature. Tables 1 and 2, below for the dissociation of Fe_2MgO_4 and Fe_2MnO_4, respectively, suggest temperatures less than 2000K might be feasible. Given the pessimistic estimates from HSC for the dissociation of Fe_3O_4, and the fact that HSC does not account for solid solutions, there is reason to be optimistic that dissociation temperatures can be reduced. In addition, there has been a great deal of theoretical and laboratory research in Japan and Europe that suggests that reduction temperatures for mixed metal oxides can be substantially reduced, compared to iron oxide alone (Refs. [5–11]).

Although much of the high temperature reduction work has been done at temperatures as low as 1300 K, they were typically conducted with a flowing inert gas, effectively reducing the oxygen partial pressure to essentially zero (Refs. [6–9]). Recently, however, Aoki, *et al*. demonstrated 0.13 moles O_2 gas release per mole $NiFe_2O_4$ in air at 1800 K (Ref. [11]). The presence of solid solutions, which are not included in HSC, is suggested as to why the oxygen generating reaction temperature is reduced. However, calculations with HSC, assuming all of the likely species, indicate oxygen generation in air at 1800 K to 1900 K. Aoki was able to regenerate the nickel ferrite in a nitrogen/steam flow at 1123 K. Simulations with HSC indicate very little hydrogen generation at this condition, suggesting that continually supplying water and removing the product hydrogen drove the hydrolysis reaction.

It is important to understand that evaluation of simple reaction equations can sometimes be misleading. If the products of a reaction dissociate or all of the possible products are not

accounted for, the extent of reaction can be much higher than the delta G of a reaction indicates. Figure 1 shows the HSC predicted equilibrium of Fe_3O_4 at 1 atm pressure which is much more inclusive of possible products than the simple reaction equation $Fe_3O_4 = 3FeO + 1/2O_2(g)$. Note that O_2 becomes appreciable at temperatures significantly less than 2000 K, despite the fact that ΔG for the reaction equation is above 0 at 3100 K.

Table 1. Thermodynamics of $Fe_2MgO_4 = 2FeO + MgO + 1/2O_2(g)$

T	deltaH	deltaS	deltaG	K	Log(K)
K	kcal	cal/K	kcal		
1000.000	73.063	33.924	39.139	2.789E-009	-8.555
1100.000	73.542	34.380	35.723	7.977E-008	-7.098
1200.000	74.000	34.779	32.265	1.328E-006	-5.877
1300.000	74.438	35.130	28.769	1.456E-005	-4.837
1400.000	74.853	35.438	25.240	1.147E-004	-3.941
1500.000	75.238	35.704	21.683	6.927E-004	-3.159
1600.000	75.588	35.929	18.101	3.368E-003	-2.473
1700.000	87.492	43.144	14.148	1.517E-002	-1.819
1800.000	87.929	43.393	9.821	6.420E-002	-1.192
1900.000	88.302	43.595	5.471	2.348E-001	-0.629
2000.000	88.613	43.755	1.103	7.576E-001	-0.121
2100.000	88.863	43.877	-3.279	2.194E+000	0.341
2200.000	89.053	43.965	-7.671	5.783E+000	0.762
2300.000	89.184	44.024	-12.071	1.403E+001	1.147
2400.000	89.258	44.055	-16.475	3.165E+001	1.500
2500.000	89.277	44.063	-20.881	6.693E+001	1.826

Inclusion of additional metal oxides of manganese, Fig. 2, and manganese and nickel, Fig. 3, further reduce the temperature requirements.

Even if reasonable oxygen partial pressures can be attained at reasonable temperatures (<1800 K) the analyses by Nakamura, Ref. [12], and Steinfeld, *et al.*, Ref. [13], suggest that unless sensible heat recovery approaches can be developed, the overall cycle thermal efficiency will be low.

To address sensible heat recovery in the Ferrite cycles, Sandia has invented a number of receiver/reactor configurations that utilize solid-to-solid thermal recuperation. An analysis was performed on the potential for achieving high conversion of solar input to higher heating value in hydrogen with these new concepts. The analysis is based on 36 kW net thermal input to the reactor and a reactor temperature in the range 1900 K to 2100 K and a pressure of 0.2 atm. The reactor design parameters are believed to be realistic of what might be achieved. Based on recent results by Kodama, Refs. [8,9], the ferrite is assumed to be impregnated on an inert carrier, zirconia, with 75% inert by weight. For the conditions modeled the amount of net hydrogen produced at 1900 to 2100 K is comparable to what Kodama reported at 1673 K [9]. However, because Kodama maintained a steady inert (nitrogen) gas flow during the thermal reduction, he shifted the equilibrium towards dissociation and his results are not directly comparable.

Table 2. Thermodynamics of $Fe_2MnO_4 = 2FeO + MnO + 1/2O_2(g)$

T	delta H	delta S	delta G	K	Log(K)
K	kcal	cal/K	kcal		
1000.000	71.972	27.716	44.256	2.124E-010	-9.673
1100.000	71.967	27.711	41.485	5.714E-009	-8.243
1200.000	72.027	27.762	38.712	8.892E-008	-7.051
1300.000	72.149	27.860	35.931	9.097E-007	-6.041
1400.000	72.330	27.994	33.139	6.705E-006	-5.174
1500.000	72.562	28.153	30.332	3.805E-005	-4.420
1600.000	72.836	28.330	27.508	1.747E-004	-3.758
1700.000	84.742	35.545	24.315	7.480E-004	-3.126
1800.000	85.252	35.837	20.745	3.027E-003	-2.519
1900.000	85.771	36.117	17.148	1.065E-002	-1.973
2000.000	86.294	36.386	13.522	3.328E-002	-1.478
2100.000	86.821	36.643	9.871	9.390E-002	-1.027
2200.000	97.881	41.868	5.771	2.671E-001	-0.573
2300.000	98.449	42.121	1.572	7.090E-001	-0.149
2400.000	99.020	42.364	-2.652	1.744E+000	0.242
2500.000	99.594	42.598	-6.901	4.011E+000	0.603
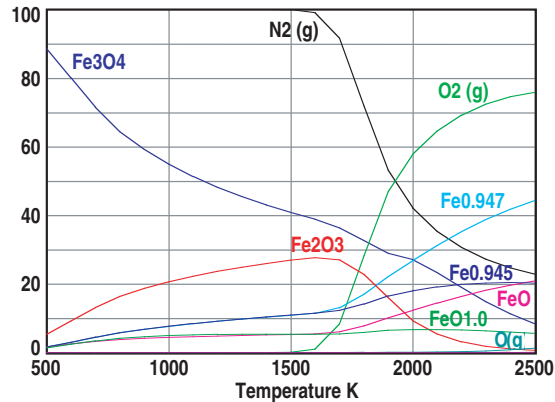
Fig. 1. Equilibrium composition, mole %, of dissociated Fe_3O_4 at 1 atm pressure as a function of temperature calculated with HSC (Ref. [2]).

The recuperator analysis assumes constant heat capacity and what are believed to be realistic heat transfer parameters. The recuperator analysis uses an iterative approach to determine the recuperator delta T, and therefore, the recuperator effectiveness. The recuperator delta T, reactant heat capacity and reactor design determine how much of the input power is needed to heat the reactants from the approach temperature to reduction-reactor temperature and how much is available for driving the reduction reaction.
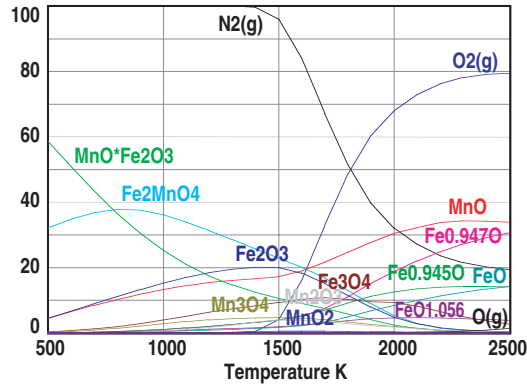
Fig. 2. Equilibrium composition, mole %, of dissociated Fe_2MnO_4 at 1 atm pressure as a function of temperature calculated with HSC (Ref. [2]).
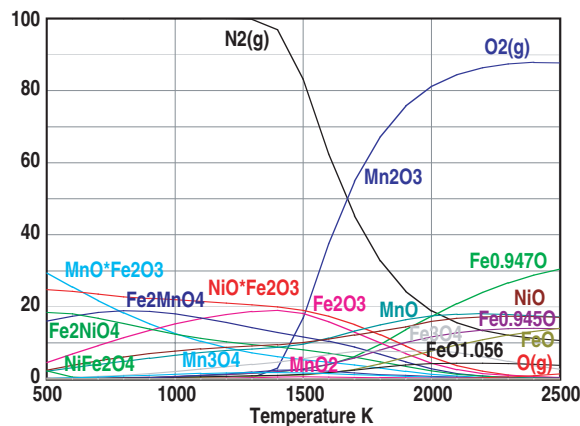
Fig. 3. Equilibrium composition, mole %, of equal amounts of dissociated Fe_2NiO_4 and Fe_2MnO_4 at 1 atm pressure as a function of temperature calculated with HSC (Ref. [2]).

The thermodynamics are based on HSC, Ref. [2], and determine the amount of oxygen and hydrogen that can be generated. The fact that the HSC results are in reasonable agreement with reported experimental results is reason to be comfortable with, if not confident in, HSC. A number of chemical systems were evaluated, including (Fe, Mn); (Fe, Mg); (Fe, Ni); (Fe, Co); and (Fe, Mn, Mg). The compositions into the high-temperature reduction reactor and hydrolysis reactor were iteratively determined using HSC. In the first iteration, the dissociated products of one mole of material at the assumed reactor temperature and 1 bar were calculated. These products, minus the free oxygen, were then reacted with one mole of H2O(g) at the assumed hydrolysis temperature, typically 600 K and 1 bar. In the next iteration the products from the hydrolysis reactor, minus the hydrogen, is reduced at the reduction reactor temperature and its products, minus oxygen, are fed into the hydrolysis reactor. Depending on the system, the compositions between iterations eventually converged or not. For the systems that converged, the resulting hydrogen production was double the oxygen production. The HSC Heat and Material balance is then utilized to determine the thermal requirements per gram of material fed into the reactor as well as the sensible heating load of the reactants and the sensible heat available from the reduced products. Because the oxygen is removed, the total sensible heat needed for heating the reactants is typically slightly higher than the sensible heat available in the solid products. In addition to heating the reactants from the recuperator to reactor temperature, the solar input must,

therefore, also provide the delta H of the reaction as well as the delta- delta H of the sensible heat between the products and reactants.

The HSC analysis suggests that the (Fe, Mg) and (Fe, Co) systems are best and that the reduction reaction temperatures needed to achieve reaction extents that are comparable to the Fe_3O_4 system can be reduced by 100 to 300 K. The (Fe, Co) system, in particular, looks very interesting, but discrepancies with the HSC thermodynamic data for cobalt ferrite ($CoFe_2O_4$) raise questions. The nickel-manganese-ferrite system called out in PID #2 is inadequately represented in HSC. Although using the chemical constituents in HSC indicates a high degree of dissociation and oxygen at temperature less than 2000 K, the products were not adept at reducing water to any significant degree.

The amount of pump work required to compress the oxygen to 1 atm and the hydrogen to 15 atm assuming 40% isothermal compression efficiency is also calculated and is utilized in the net efficiency calculation assuming a conversion of heat to work efficiency of over 50% are feasible.

Table 3 is a summary showing the effect of chemical system, operating temperature, reaction extent, inert fraction, and recuperator heat transfer relative to our baseline design. **These results indicate that efficiencies of over 50% are theoretically feasible if optimistic estimates are assumed.** The parametric results are for three metal oxide systems (Fe O), (Fe Mg O), and (Fe Co O); at various temperatures; reaction extents; recuperator heat transfer factors; and inert fractions (zirconia weight fraction). In the table the reaction extent and the equilibrium reaction extent are listed. The equilibrium reaction extent refers to the percentage of hydrogen, per mole of ferrite calculated iteratively with HSC, as described above. The reaction extent is the moles of hydrogen per mole of ferrite in the simulation. The recuperator factor is relative to our baseline design. Numerous approaches for enhancing heat transfer are possible. The results indicate that reducing the amount of inactive material, either inert or un-reacted ferrite, is key to high efficiency. Enhancing recuperation heat transfer also helps thermal efficiency.

These cycles have unique advantages of simplicity, direct heating of solids, inherent separation of the product oxygen and hydrogen, and avoid the use of corrosive chemicals. If either the thermodynamics can be shown to improve as a result of mixing metal oxides, ways to work at low hydrogen and oxygen generation pressures, or materials issues associated with very high temperatures (>2000 K) can be solved, then this class of thermodynamic cycles is very attractive.

Table 3. Summary results of metal oxide thermodynamic analysis

Chemical System	Temp, K	Reaction Extent	Equil. Extent	Recup. Factor	Inert Fraction	Efficiency
Fe O	2300	0.36	0.36	1X	0.75	33.8%
Fe O	2300	0.36	0.36	2X	0.75	40.0%
Fe O	2300	0.50	0.36	1X	0.75	40.3%
Fe O	2300	0.19	0.36	1X	0	40.1%
Fe O	2300	0.24	0.36	2X	0	50.9%
Fe Mg O	2100	0.27	0.27	1X	0.75	31.5%
Fe Mg O	2100	0.27	0.27	2X	0.75	37.3%
Fe Mg O	2100	0.42	0.27	1X	0.75	39.7%
Fe Mg O	2100	0.22	0.27	1X	0	46.1%
Fe Mg O	2100	0.26	0.27	2X	0	53.3%
Fe Co O	2100	0.55	0.55	1X	0.75	39.5%
Fe Co O	2100	0.54	0.55	2X	0.75	43.9%
Fe Co O	2100	0.72	0.55	1X	0.75	43.4%
Fe Co O	2100	0.24	0.55	1X	0	43.1%
Fe Co O	2100	0.27	0.55	2X	0	48.4%
Fe Co O	1900	0.27	0.27	1X	0.75	28.6%
Fe Co O	1900	0.27	0.27	2X	0.75	33.5%
Fe Co O	1900	0.40	0.27	1X	0.75	34.7%
Fe Co O	1900	0.14	0.27	1X	0	38.2%
Fe Co O	1900	0.27	0.27	2X	0	47.8%

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PID 4 –IRON CHLORIDE-1

This assessment is based on modifying the MARK 9 cycle as a hybrid with an electrochemical reactor for the FeCL2-5 reaction as follows:

Reaction Code	Formula (PID 4 – MARK 9)	Multiplier	Max. Temp. (^{o}C)
FeCl2-5	$3FeCl_2(a) + 4H_2O(l) = Fe_3O_4 + 6HCl(a) + H_2(g)$	1	100 (electrochemical)
Cl2-5	$2Fe_3O_4 + 12HCl(g) + 3Cl_2(g) = 6FeCl_3(s) + 6H_2O(g) + O_2(g)$	0.5	50
FeCl3-1	$6FeCl_3(g) = 6FeCl_2(s) + 3Cl_2(g)$	0.5	420

SUMMARY

The solar heating requirement reduces the calculated MARK 15 cycle efficiency to 33.8%, not including the electrochemical requirement. Therefore, further consideration of the MARK 15 hybrid cycle appears unjustified.

DISCUSSION

It should be noted that complicated and expensive reactors and heat exchangers are required for these conditions to deal with high-temperature gases and the melting and boiling points of the reactants, such as:

Compound	MP	BP
FeCl2	677 C	1023 C
FeCl3	304 C	316 C

A UNLV reaction code matrix for Fe-Cl cycles is attached. The FeCL2-5 (electrochemical) and FeCl3-1 reactions are common to the MARK 7, 7a, 7b (PID 22), MARK 9 (PID 4) and MARK 14 cycles. HSC-5 data were prepared for these reactions for the PID 22 – MARK 7b assessment, which show that the FeCL3-1 reaction is exothermic, requiring heat to be removed from the reactor. HSC-5 data for the Cl2-5 reaction show delta G is negative below 223°C.

Experimental data showed that reaction Cl2-5 produces no oxygen below 223 C, but oxygen was produced at high temperature. Therefore the PID 4 – MARK 9 cycle does not work either with or without an electrochemical hydrogen production step [1].

This resulted in splitting the Cl2-5 reaction into the Cl2-1 reaction and a new reaction in the MARK 14 cycle [1], which can be shown as a hybrid cycle, as follows:

Reaction Code	Formula (No PID – MARK 14)	Multiplier	Max. Temp. (ºC)
FeCl2-5	3FeCl2(a) + 4H2O(l) = Fe3O4 + 6HCl(a) + H2(g)	1	100 (electrochemical)
Cl2-1	2Cl2(g) + 2H2O(g) = 4HCl(g) + O2(g)	0.5	800
FeCl3-1	6FeCl3(g) = 6FeCl2(s) + 3Cl2(g)	0.5	420
Fe2O3-1	Fe2O3 + 6HCl(g) = 2FeCl3(s) + 3H2O(g)	1.333	100
NEW	6Fe3O4 + 3Cl2(g) = 8Fe2O3 + 2FeCl3(g)	0.167	420

HSC-5 data for the Cl2-1 reaction show delta G is negative above 595°C and negative between 316 and 1449 C for the NEW reaction. A further problem was discovered in the FeCl3-1 decomposition step [2], where delta G is negative for this exothermic reaction in three operating ranges: endothermic above 1403°C, where the reactants are gases; exothermic between 677°C and 1023°C, where the FeCl2 is a liquid; and exothermic between 316°C and 572°C, where FeCl3 is a gas. Operating in the low-temperature range allows about 240 MJ to be used to produce steam at about 390°C. With a counter-flow input/output heat exchanger, the NEW reaction requires 477 MJ plus heat leak per kg-mole of H2 produced.

The MARK 14 cycle requires five consecutive cyclic reactions, where the solid mass flows are up to 505 kg/mole of H2 produced. An early assessment concluded that the MARK 9 and MARK 14 cycles contain equilibrium reactions that substantially limit the degree of conversion [1]. However, the MARK 14 cycle requires lower temperatures than the PID 22 MARK 7b cycle and may require less expensive materials for exposure to the required conditions.

Using an electrochemical step for the FeCl2-5 reaction and a solar heater to produce gaseous feed to the Fe2O3 reactor, the calculated MARK 14 cycle efficiency is 41.5%, not including the electrochemical requirement. Therefore, further consideration of the MARK 14 hybrid cycle appears unjustified.

The simpler modified MARK 15 cycle can be characterized by the following reactions:

Reaction Code	Formula (No PID – MARK 15)	Multiplier	Max. Temp. (ºC)
FeCl2-5	3FeCl2(a) + 4H2O(l) = Fe3O4 + 6HCl(a) + H2(g)	1	100 (electrochemical)
Cl2-1	2Cl2(g) + 2H2O(g) = 4HCl(g) + O2(g)	0.5	800
FeCl3-1	2FeCl3(g) = 2FeCl2(s) + Cl2(g)	1	420
Fe3O4-5	Fe3O4 + 8HCl(g) = FeCl2(s) + 2FeCl3(s) + 4H2O(g)	1	200

The MARK 15 cycle requires four consecutive cyclic reactions, where the solid mass flows are reduced to 260 kg/mole of H2 produced. However, a 664 MJ solar heater is required to

vaporize 8 moles of HCl(a) produced by the FeCl2-5 reactor and the Cl2-1 reactor (for separation of oxygen) for introduction to the Fe3O4-5 reactor.

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PID 5 – HYBRID CADMIUM

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (°C)
Cd	$Cd + 2H_2O(g) = Cd(OH)_2 + H_2(g)$	1	25
Cd(OH)2	$Cd(OH)_2 = CdO + H_2O$	1	375
CdO	$2CdO = Cd + O_2(g)$	0.5	1200

CONCLUSIONS:

This cycle is not technically feasible at a maximum temperature of 1200°C. With heat recovery and batch operation, efficiency is about 55% if a solar heater can provide 1600°C to the CdO reactor, but operating costs may be $30/mole of H2 due to inert gas consumption.

DISCUSSION

HSC-5 data for the Cd reaction indicate delta G < 0 between 60°C and 351°C, with very slow kinetics. Therefore this reaction was proposed as an electrochemical step [1]. Experimental work indicated current densities of about 30 mA/cm^2 were achieved at an electrode overpotential of 80 mV in 5N NaCl electrolyte between 56 and 70°C. Mixing the anolyte and catholyte solutions was required in a separate vessel to provide the required Cd(OH)2. The source energy required for this step is 28 MJ per kg mole of H2 and the proposed operating temperature should be above 56°C.

HSC-5 data for the Cd(OH)2 reaction show delta G < 0 above 128°C. The maximum duty for the reactor is 90 MJ for discharge at the proposed temperature per kg mole of H2 with dry feed, requiring a input/output heat exchanger to handle moisture associated with the Cd(OH)2 and condensing of the produced water for recycle to the electrochemical step.

HSC-5 data for the CdO reaction show delta G < 0 above 2303°C, while the reverse reaction is highly favored below that temperature. Testing indicated that the reaction could be completed in a stream of inert carrier gas such as argon between 1350 and 1610°C [1]. The carrier gas was necessary to drive the reaction and sweep the oxygen from the reactor before it oxidized the Cd that was produced as a coating on a water-cooled condenser. When counter-flow input-output heat exchanger is used, the duty for this reactor is 355 MJ per mole of H2 at 1600°C and 1 mole of argon carrier gas.

The carrier gas cannot easily be separated from oxygen for recycle to the CdO reactor, so operating costs should reflect purchase of at least one mole of Ar per mole of H2 produced at a

cost of about \$30/mole. The reactor would have to be operated in batch mode to provide a means for separating and removing Cd metal from the water-cooled condenser.

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PID 6 – ZINC-ZINC OXIDE

This process is based on the following chemical reactions:

Reaction Code	Formula	Multiplier	Temp (°C)
Zn	Zn + H2O = ZnO(s) + H2(g)	1	900
ZnO	2ZnO(s) = 2Zn + O2(g)	0.5	2200

CONCLUSIONS

This cycle is estimated to have an efficiency of ~45% (LHV).

DISCUSSION

Fluid Wall Reactor

The proposed flowsheet for the process is shown in Fig. 1. A good starting point for the process description is the ZnO decomposition reactor. The ZnO decomposition reaction takes place at ultra-high temperatures (2000 K – 2300 K). Solar energy provides the necessary power, giving high energy intensities (> 1000 W/cm^2) and heating rates (~10^6 K/s). Sub-micron sized ZnO particles are carried by an inert gas, chosen to be helium for its relative ease of separation from O$_2$. Re-radiation losses from the hot graphite tube are calculated by assuming that the reactor design is comparable to a cavity receiver. From previous experimental work, it is chosen that 1/3 of the helium flow is used for particle entrainment and 2/3 of the helium flow is used in the "fluid wall".

Product Quench and Helium Recycle Preheating

Exiting the decomposition reactor, the product stream is rapidly cooled to prevent recombination of Zn with O$_2$ and to aid in nano-sized Zn particle formation. The base scenario assumes that the net conversion to Zn is 80% leaving this reactor. This number is consistent with the laboratory results. The molar ratio of inert gas to ZnO flow is a key design variable. The actual minimum requirement of inert gas flow for ZnO particle entrainment is unknown and is presently being determined as a part of the experimental program at the University of Colorado. The base scenario sets the ZnO decomposition reaction at 1 bar. A portion of the product enthalpy is recovered by preheating the feed stream of helium to 1100 K in a gas preheating heat exchanger.

Heat Recovery

To increase the energy efficiency of the thermochemical cycle, some method must be devised to efficiently capture the heat from the cooling product stream and convert that heat into a

useable form. As of yet, the authors have not designed or modeled a heat exchanger to maximally collect heat from the product stream of the decomposition reaction under the constraint that this stream must be cooled quickly enough to prevent recombination of the products. This heat exchanger must cool the products from reactor exit temperature to gas separation temperature in one unit, allowing for nucleation of the zinc solid product. Design of this heat exchanger will require knowledge of the reaction rates for the recombination reaction of Zn and O_2, as well as particle nucleation and size distribution information for the Zn solid product.
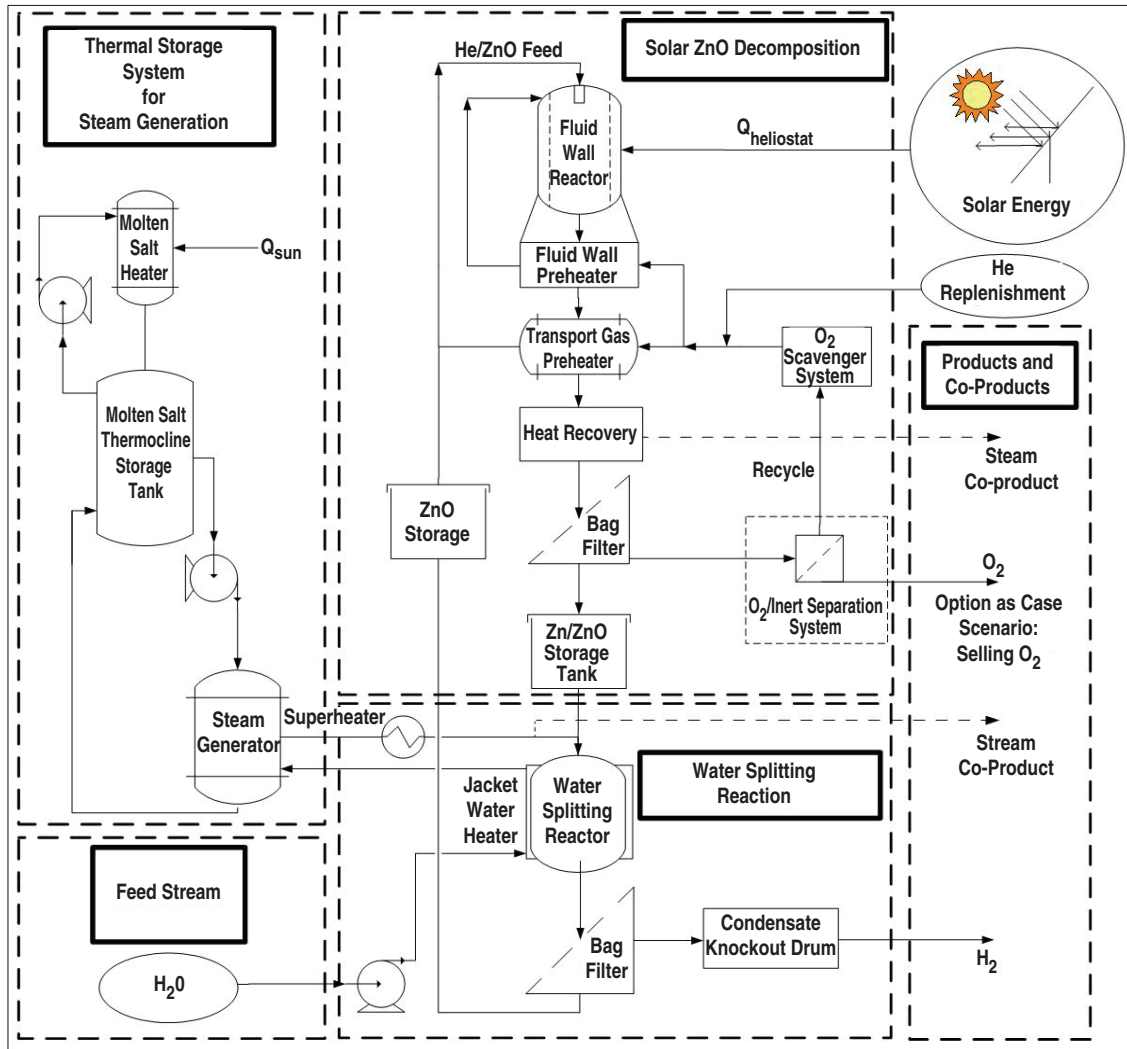
Fig. 1. Process flow diagram.

Due to this lack of a working design, the authors have made a base assumption about how much heat may be collected from the product stream. Due to the rate of product cooling required to prevent recombination, it has been assumed that the cooling process for reactor exit temperature to 1200 K yields no usable heat. Below 1200 K, heat can be transferred to other streams as in a countercurrent heat exchanger. This assumption was based on the kinetic prohibition of reverse reaction below 1200 K, but is mainly an approximation. Surely, some usable heat will be collected between 1200 K and reactor exit temperature, and heat collection

below 1200 K will not be ideal. Still, this approximation of the actual heat exchange will be a conservative estimate, and should give a value expected to be an operating low-end for the thermal recovery efficiency.

Oxygen Removal

The Zn nanoparticles are recovered in a bag filter and a 3-stage Vacuum Swing Absorption (VSA) unit separates the helium-oxygen product stream. Trace amounts of oxygen in the helium recycle stream are removed in an oxygen-scavenging unit that is periodically regenerated with a small stream of hydrogen. 0.3% of the Helium is lost to the vent O_2, and must be replenished with additional helium. To regenerate the copper scavenger, about 2% of the product H_2 must be fed during the regeneration process.

Water-splitting Reaction

After leaving the gas/solid separator, product Zn is stored in a bin. From this bin, it is pressurized and fed to a reactor with saturated steam at 23 bar (saturation temperature = 501.15 K). According the thermodynamics, the water-splitting reaction [Eq. (2)] goes to completion at this temperature. A bag filter separates the nanosized ZnO particles, which are fed to the solar decomposition reactor to complete the cycle. The product hydrogen is produced at elevated pressure, minimizing the need for delivery compression. A condensate flash drum removes any remaining water.

Molten Salt Thermocline System

While electricity is used for steam generation in the base economic analysis, stored solar thermal energy could provide an "all-solar" option for running this process. Feed water, pressurized to 35 bar, cools the Zn-H_2O reactor in a jacketed tank and exits at a temperature near 509 K. A secondary power tower system provides the latent heat required to vaporize the preheated water. A stoichiometric amount of the steam enters the Zn-H_2O reactor and the excess steam is sold as steam to a nearby utility user. The secondary power tower system uses molten solar salt (60%-40% $NaNO_3$-KNO_3) as a heat transfer fluid [13]. A thermal storage tank stores enough heat for 24-hour steam production. An electric heater raises the steam temperature to 814 K. This system allows both steam and Zn powder to enter the water-splitting reactor at 600 K.

Material and Energy Balances

This boundary analysis is restricted to thermodynamic calculations, made possible using FACT-Sage thermochemical data. A simplified version of the program is available on the World Wide Web. The material and energy balances are solved using a combination of enthalpy calculations in EXCEL® for the high temperature reaction and ASPEN®-PLUS for the remainder of the process. Economic assumptions are set to be compatible with U.S. Department of Energy H2A standards, which have been proposed to make various hydrogen production technologies and scenarios more directly comparable. The production of hydrogen is set to 150,000 kg H_2/ day, corresponding to a large central production facility (supplying an estimated 225,000 hydrogen fuel cars). Optimal heliostat field sizes will not reach the total field size

required to produce 150,000 kg H_2/day. Therefore, a 150,000 kg H_2/day production facility will demand several power tower fields that feed into a common storage area and into a single water splitting reactor.

Heliostat Field

As a first estimate, the size of the heliostat field is calculated based on the experimental setup at the National Renewable Energy Laboratory (NREL), where 1700 m^2 of heliostat mirror area provide 1.1 MW_{th} to the solar reactor. The measured optical efficiency of the heliostats, $\eta_{optical}$, corresponds to about 70%. The calculated thermal energy consumed in the reactor dictates the size of the heliostat field. The annual beam irradiation is assumed to be 2300 kWh_{th}/m^2/yr, and the equivalent full power hours equals 2300 h.

Fluid Wall Reactor

The enthalpy requirement for the reaction is calculated by the following:

$$\Delta H \big|_{ZnO(s)} + x \cdot He \text{ (at 300 K)} \rightarrow Zn(s) + x \cdot He + 1/2O_2 \text{(at reactor temperture)} \quad . \quad (1)$$
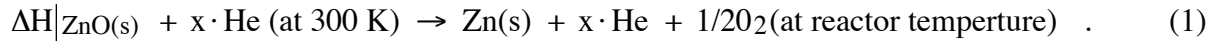
The reactor temperature was set equal to the temperature for complete conversion, which is a function of the He/ZnO molar ratio, and was calculated by FACT-Sage®. The total energy required to be provided by the heliostat field is found by assuming that the reactor is a black-body cavity-receiver, with no conduction or convection heat losses and absorptivity and emissivity equal to 1:

$$Q_{heliostat} = 1 - \left(\frac{\sigma T^4}{IC}\right)^{-1} \cdot Q_{reactor, \, net} = \eta_{absorption} \cdot Q_{reactor, \, net} \quad . \quad (2)$$

For this study, I, the normal beam insolation, is taken to be 1 kW/m^2C, and the flux concentration ratio is set to 5000 suns. T is the reactor temperature and σ is the Stefan-Boltzmann constant. The energy loss due to reradiation is then calculated from a simple energy balance: $Q_{reradiation} = Q_{heliostat} - Q_{reactor}$. For this reactor, this energy loss is on the order of 26% for the 1:1 Zn/Inert feed ratio.

Quench Losses

In light of the heat exchanger assumption stated above, all sensible product heat between reactor exit temperature and 1200 K is assumed to be lost. This is calculated from:

$$Q_{quench} = \dot{n}\Delta H \big|_{Zn+0.5O_2+xHe \text{ (at reactor temp)}} \rightarrow (1\text{-}\zeta_{conv})ZnO + \zeta_{conv} \cdot Zn + 1/2 \cdot \zeta_{conv} \cdot O_2 + xHe \text{ (at 1200 K)} \quad . \quad (3)$$

Here, ξ_{conv} is the net extent of reaction, equal to 0.8 in the base economic case.

Heat Recovery

Upon further cooling, the product stream is assumed to heat up the recycled helium to 1100 K. Preheating the helium reduces the size requirements for the heliostat field. The remaining energy, $Q_{recoverable}$, that could be used to provide heat for steam production is assumed to be equal to the enthalpy difference between the product stream at 1180 K to 500 K, multiplied by the Carnot efficiency. The energy loss from 500 K to 300 K is assumed to be lost. However, this heat could be used to preheat water.

$$Q_{recoverable} = \left(1 - \frac{300 \cdot K}{1200 \cdot K}\right) \cdot \Delta H \Big|_{\substack{(1-\xi_{conv}) \cdot ZnO + \xi_{conv} \cdot Zn + 1/2(\xi_{conv}) \cdot O_2 + xHe \quad (\text{at } 1200\,K) \\ \rightarrow (1-\xi_{conv}) \cdot ZnO + \xi_{conv} Zn + 1/2(\xi_{conv}) \cdot O_2 + xHe \quad (\text{at } 300\,K)}} \tag{4}$$

Inert/O$_2$ Separation

A Vacuum Swing Adsorption (VSA) system has been selected to perform the necessary separation of inert He and O$_2$ product gas following the ZnO decomposition reaction. Based on estimates from other manufacturers, membrane separation units would not be able to provide the necessary purity required for the He/O$_2$ separation. A Pressure Swing Adsorption (PSA) system, using current technology, also would not meet the design requirements. Although more costly to build and run, a VSA can perform the separation within the design requirements.

The pressure requirements and capital investment for the VSA system were provided by QuestAir Technologies, Inc, given a worst-case 1:1 He/O$_2$ feed ratio to the VSA. The estimated inlet pressure was quoted to be 9 bara, with an outlet of 8 bara and an exhaust of 0.5 bara. The estimated recovery of He is 85% in one stage, with 99% purity. With a three-stage system, >99% recovery is estimated. True inlet pressure requirements, as well as more complete VSA design, require more complexity than what this study warrants. Improvements in the separation technology will affect the economics in two significant ways. First, electric utility costs will be decreased. Second, compressor capital costs for pressuring the product gas will be siginifically decreased.

Water-Splitting Reaction

According to the DOE H2A current economic assumptions, "plant gate" H$_2$ must be compressed to 300 psig (21.7 bar). There is no requirement for on-site storage. The Zn-H$_2$O reaction is thermodynamically favored ($\Delta G < 0$) above 300 K. Due to the nano-scale size of the Zn particles, the kinetics of the reaction with steam are expected to be fast. This reaction is likely mass transfer limited, with the slow step being the diffusion of water to the Zn particle surface. The nano-scale Zn powder has a much higher surface area to mass ratio than bulk Zn, suggesting a major decrease in mass transfer resistance. Fast kinetics have been shown in the literature to require a particle size less than 1–10 μm. However, more experiments must be performed to verify this assumption.

A significant reduction in product gas compression costs can be achieved by running this reaction at high pressure, shifting the compression load to liquid water. At 226.85°C (501.15 K) and 23 bar, the water-splitting reaction is exothermic, with ΔH_{rxn} = -106 kJ/mol. The energy

required to heat and vaporize water at 23 bar, is ΔH = -50.8 kJ/mol. For this scoping analysis, the reaction is assumed to go to the equilibrium conversion. The exothermic energy of the second reaction is recuperated and used to preheat the water feed to the reaction. This water then flows to a steam generator, with the necessary heat provided either by electrical heaters or molten salt from the thermocline/secondary receiver.

Molten Salt Heat Storage Requirements

The energy rate needed for the secondary power tower thermal system, with thermocline storage, was calculated in ASPEN® PLUS as the latent energy requirement for producing steam for the water-splitting reaction. Since more water is preheated than required for the reaction, extra steam is produced at high pressure and can be sold for a co-product credit of $7.88/1000 kg of high-pressure steam, as specified in the DOE H2A protocol.

A thermocline thermal storage tank is a more economical way of storing energy than a two tank salt system. A thermal gradient, supported by lower-cost filler material and buoyancy forces, separates the hot fluid from the cold fluid. A description of such a thermal system is found in the literature.

Process Efficiency Estimation

From material and energy balances, the thermal solar energy requirement for the reactor is estimated to be 2400 MW for the 1:1 He/ZnO molar ratio case, assuming the ZnO dissociation reaction takes place at a pressure of 1 bar. Energy costs, mostly arising from gas compression, come to 170 MW. The energy content of the H_2 produced is 746 MW (using the value of 241 kJ/mol H_2 LHV). Heat recuperated in the process with no direct process use can be turned into useful work, using the Carnot efficiency as an idealization. This useful energy is found to be 380 MW. Assuming no heat recovery beyond that used to preheat the helium feed stream, the efficiency is estimated by:

$$\eta_{process} \text{ (no heat recovery)} = \frac{\text{Energy value of } H_2}{\text{Solar energy into fluid wall reactor} + \text{Energy Cost of Separation}} \tag{5}$$

If an attempt is made to recover the heat, the efficiency is calculated by:

$$\eta_{process} \text{ (with heat recovery)} = \frac{\text{Energy value of } H_2 + \eta_{Carnot} \cdot \text{Heat energy recoverable}}{\text{Solar energy into fluid wall reactor} + \text{Energy Cost of Separation}} \tag{6}$$

For the base case scenario, the efficiency varies between 22%–38% for no heat recovery to total Carnot heat recovery. This efficiency does not include mirror losses of the heliostats. **If re-radiation losses are ignored, as in the other analyses in the SHGR program, this efficiency increases to 45%.** The theoretical efficiency will be higher with better decomposition conversion, less strict quench requirements, or a less energy intensive gas separation process. The process will certainly have a higher efficiency when the 6:1 $He:O_2$ ratio is applied to VSA design and specification the current estimates for a 1:1 $He:O_2$ separator feed stream ratio.

PID 7 –IRON OXIDE

The Iron Oxide, a.k.a. Muravlev cycle is based on the following two reactions from Ref. [1].

Reaction Code	Formula	Multiplier	Proposed Temp. (°C)
Fe3O4-7	2Fe3O4 = 6FeO + O2(g)	0.5	2200
FeO-1	3FeO + H2O = Fe3O4 + H2(g)	1	700

Calculations using HSC, Ref. [2], indicate a positive delta G even at temperatures as high as 3000 K. Data from JANAF Thermochemical Tables, Ref. [3], indicate negative delta G at temperatures substantially less than 3000 K and the Facility for the Analysis of Chemical Thermodynamics (FACT) (Ref. [4]) indicates a negative delta G at a temperature 365 K less than HSC. Although HSC predicts appreciable dissociation at less than 2500 K when all of the major reaction products are considered, Sibieude (Ref. [6]) measured considerably higher conversions in air at 1900°C (2173) than predicted by HSC.

Analysis by Nakamura, Ref. [5], indicates that efficiencies over 90% are theoretically feasible at 2500 K with complete conversion of Fe3O4 to FeO if most of the sensible heat in the dissociated products can be recovered. With no heat recovery, the maximum theoretical efficiency is less than 40%. Nakamura suggested a heat recovery approach that utilizes a gas heat exchange medium. Steinfeld, *et al.*, Ref. [7], utilized JANAF to determine conversion extent and came to similar conclusions. With sensible heat recovery, overall system efficiencies, including solar collection and efficiency based on delta G (not delta H) of over 50% are possible. Without sensible heat recovery, the overall system efficiency would be about 20%.

To address sensible heat recovery in the Iron Oxide and similar cycles, Sandia has invented a number of receiver/reactor configurations that utilize solid-to-solid thermal recuperation. An analysis was performed on the potential for achieving high conversion of solar input to higher heating value in hydrogen. The analysis is based on 36 kW net thermal input to the reactor and a reactor temperature and pressure of 2300 K and 0.2 atm, respectively. The reactor design parameters are believed to be realistic of what might be achieved. Based on recent results by Kodama, Refs. [8,9], the iron oxide is assumed to be impregnated on an inert carrier zirconia with 75% inert by weight in the analysis. For the condition modeled the amount of net hydrogen produced at 2300 K is comparable to what Kodama reported at 1673 K [9]. However, because Kodama maintained a steady inert (nitrogen) gas flow during the thermal reduction, he shifted the equilibrium towards dissociation and his results are not directly comparable.

The recuperator analysis assumes constant heat capacity and what are believed to be realistic heat transfer parameters. The recuperator analysis used an iterative approach to determine the recuperator delta T, and therefore, the recuperator effectiveness. The recuperator delta T, reactant heat capacity and reactor design determine how much of the input power is needed to heat the

reactants from the approach temperature to 2300 K and how much is available for driving the reduction reaction.

The thermodynamics are based on HSC, Ref. [2], and determine the amount of oxygen and hydrogen that can be generated. There is a great deal of uncertainty regarding the thermodynamics of the iron oxide and related metal oxide cycles. Discrepancies with other thermochemical programs, uncertainty with regard to the species to select, as well as effects of solid solutions make the thermodynamics in the analysis uncertain. The fact that the HSC results are in reasonable agreement with reported experimental results is reason to be comfortable with, if not confident in, HSC. The compositions into the high-temperature reduction reactor (2300 K) and hydrolysis reactor (600 K) are iteratively determined using HSC. In the first iteration, the dissociated products of one mole Fe_3O_4 at 2300 K and 1 bar is calculated. These products, minus the free oxygen, are then reacted with one mole of $H2O(g)$ at 600 K and 1 bar. In the next iteration the products from the hydrolysis reactor, minus the hydrogen, is reduced at 2300 K and its products are fed into the hydrolysis reactor. Because the compositions of the first and second hydrolysis reaction are identical, the second reduction products and the first hydrolysis products are the assumed constituents. The resulting hydrogen production is 0.349 moles per mole of Fe3O4. The oxygen production is 0.174 moles—one-half the hydrogen production. The HSC Heat and Material balance is then utilized to determine the thermal requirements per gram of material fed into the reactor as well as the sensible heating load of the reactants and the sensible heat available from the reduced products. Because the oxygen is removed, the total sensible heat needed for heating the reactants is slightly higher than the sensible heat available in the solid products. In addition to heating the reactants from the recuperator to reactor temperature, the solar input must, therefore, also provide the delta H of the reaction as well as the delta- delta H of the sensible heating of the products and reactants.

The amount of pump work required to compress the oxygen to 1 atm and the hydrogen to 15 atm assuming 40% isothermal compression efficiency is also calculated and is utilized in the net efficiency calculation assuming a conversion of heat to work efficiency of 40%. Heat flows and an energy balance analysis are also included in the results.

Simulations results indicate that efficiencies of about 40% are theoretically feasible. The efficiency predicted is a strong function of the extent of reaction and the heat transfer within the recuperator. **With optimistic assumptions, an efficiency of 50% appear to be feasible.** With conservative assumptions, efficiencies of over 30% are predicted. For the Iron-oxide cycle, the high temperatures required are an issue. The incorporation of mixed metal oxides, including iron, as in PIDs #2 and #194 may be a way to reduce the temperature requirements.

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PID 9 – MANGANESE-CARBON

This process is based on the following chemical reactions:

Reaction Code	Formula	Multiplier	Proposed Temp. (°C)
Mn2O3	$6Mn_2O_3 = 4Mn_3O_4 + O_2(g)$	0.5	977
Steam/carbon	$C + H_2O(g) = CO(g) + H_2(g)$	1	700
Mn3O4	$CO + Mn_3O_4 = C + 3Mn_2O_3$	1	700

CONCLUSIONS

The proposed Mn3O4 reactor does not produce a temperature at which delta G is zero. The reaction is unfavorable at all temperatures, as shown in the HSC 5 output file in Table 1 below. This problem remains if steam is used to oxidize the Mn3O4 to Mn2O3. Therefore, the PID 9 cycle is unworkable.

DISCUSSION

HSC 5 data show that the Mn2O3 reactor must be operated above 915°C, where delta G is zero. The reactor must be designed to accommodate release of oxygen at reactor temperature and recovery of over 14 MJ/mol from this stream to increase efficiency.

A separate reactor is required for the Steam/carbon reaction, similar to a coal gasifier. Equilibrium in the COH system among CO, H2O, CO2, CH4, and H2 does not favor a mixture of 50 mol% H2 and 50 mol% CO below a temperature of about 900°C [1]. Extensive heat recovery and separation of the H2 and CO are required for hydrogen production and use of the CO in this scheme. This is usually accomplished by a water-gas shift reactor that produces CO2 and additional H2, followed by CO2 absorption, to produce a pure hydrogen stream. The CO2 could then produce CO from carbon in a separate reactor operating at about 900°C [1].

The proposed Mn3O4 reactor does not produce a temperature at which delta G is zero. The reaction is unfavorable at all temperatures, as shown in the HSC 5 output file in Table 1 below. This problem remains if steam is used to oxidize the Mn3O4 to Mn2O3. Therefore, the PID 9 cycle is unworkable.

It should be noted that replacing Mn2O3 with MnO results in a two-step process that eliminates the carbon gasification step. That dissociation reaction also has a positive delta G at all temperatures and results in sufficiently low yields not to be considered [2].

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Table 1. Reaction Mn3O4 Delta G Calculations

CO(g) + 2Mn3O4 = C + 3Mn2O3

T	deltaH	deltaS	deltaG	K	Log(K)	
C	**kJ**	**J/K**	**kJ**			
0.000	15.658	-171.183	62.416	1.156E-012	-11.937	
100.000	15.269	-172.449	79.618	7.144E-012	-11.146	
200.000	15.412	-172.129	96.855	2.026E-011	-10.693	
300.000	15.929	-171.148	114.022	4.051E-011	-10.392	
400.000	16.716	-169.887	131.075	6.731E-011	-10.172	
500.000	17.700	-168.527	147.996	1.001E-010	-10.000	
600.000	18.828	-167.156	164.780	1.385E-010	-9.859	
700.000	20.077	-165.803	181.428	1.823E-010	-9.739	Proposed reactor temp.
800.000	21.434	-164.476	197.942	2.315E-010	-9.635	
900.000	22.892	-163.178	214.324	2.860E-010	-9.544	
1000.000	24.443	-161.910	230.578	3.460E-010	-9.461	
1100.000	26.083	-160.670	246.707	4.116E-010	-9.386	
1200.000	-8.056	-184.283	263.421	4.559E-010	-9.341	
1300.000	-4.305	-181.824	281.731	4.412E-010	-9.355	
1400.000	0.519	-178.854	299.769	4.371E-010	-9.359	
1500.000	6.415	-175.435	317.487	4.431E-010	-9.354	
1600.000	13.379	-171.617	334.843	4.590E-010	-9.338	
1700.000	21.410	-167.442	351.799	4.855E-010	-9.314	
1800.000	30.508	-162.947	368.321	5.237E-010	-9.281	
1900.000	40.672	-158.160	384.378	5.757E-010	-9.240	
2000.000	51.902	-153.110	399.944	6.441E-010	-9.191	

Mn3O4		Extrapolated from		1835.000	K
Mn2O3		Extrapolated from		1400.000	K

Formula	FM	Conc.	Amount	Amount	Volume	
	g/mol	**wt-%**	**mol**	**g**	**l or ml**	
CO(g)	28.010	5.768	1.000	28.010	22.414	l
Mn3O4	228.812	94.232	2.000	457.623	94.550	ml
	g/mol	**wt-%**	**mol**	**g**	**l or ml**	
C	12.011	2.473	1.000	12.011	4.584	ml
Mn2O3	157.874	97.527	3.000	473.623	105.249	ml

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PID 14 – SODIUM-MANGANESE-1

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Proposed Temp. (°C)
Mn2O3-1	Mn2O3 + 4NaOH = 2Na2O.MnO2 + H2(g) + H2O(g)	1	800
MnO2	4MnO2(s) = 2Mn2O3(s) + O2(g)	0.5	487
Na2O-1	Na2O.MnO2 + H2O = 2NaOH(a) + MnO2(s)	2	100

CONCLUSIONS

Since the Mn2O3-1 and MnO2 reactions are not technically feasible, this cycle is not technically feasible. No efficiency can be calculated based on the Mn2O3-1 reaction, for which there is no temperature at which delta G = 0 and an electrochemical reaction is not feasible.

DISCUSSION

Mn2O3-1 Reactor

This reaction is unique to this cycle. Neglecting the heat of formation of the binary compound by separating 2Na2O + MnO2, HSC-5 data show delta G does not approach zero at any temperature. HSC-5 equilibrium data show a small amount of oxygen is generated above 1000°C, and MnO is the dominant form above that temperature. Since all forms of Mn oxides are insoluble, an electrochemical step will also not work, therefore this reaction is not technically feasible.

MnO2 Reactor

The MnO2 reaction is also proposed in PIDs 15, 82, 83, 105 and 168. HSC-5 data for the MnO2 reaction show delta G < 0 above 510°C, with adequate kinetics above about 600°C. HSC-5 equilibrium data show significant quantities of Mn3O4 and unreacted MnO2 above 600°C, therefore this reaction is not technically feasible as proposed.

Na2O-1 Reactor

This reaction is unique to this cycle. HSC-5 data show delta G < 0 at all temperatures. HSC-5 equilibrium data show complete reaction below 300°C. Production of aqueous NaOH would have required significant heat to deliver NaOH liquid or gas to the Mn2O3-1 reactor.

PID 16 – VANADIUM OXYCHLORIDE-1

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Proposed Temp. (°C)
Cl2-1	$2Cl_2(g) + 2H_2O(g) = 4HCl(g) + O_2(g)$	0.5	800
VOCl2	$2VOCl_2 + 2HCl = 2VOCl_3 + H_2$	1	170
VOCl3	$2VOCl_3 = Cl_2(g) + 2VOCl_2$	1	200

CONCLUSIONS

Since the VOCl2 and VOCl3 reactions are not technically feasible, this cycle is not technically feasible. No efficiency can be calculated based on the VOCl3 reaction, for which there is no temperature at which delta G = 0 and an electrochemical reaction is not feasible.

Cl2-1 Reactor

This is the reverse Deacon reaction, which is also proposed in many other cycles, including cycles 53, 56 and 103, which were selected for assessment. HSC-5 data show delta G is negative above 595°C. HSC-5 equilibrium data show about 1.2 moles of HCl(g) and 0.3 moles of O2(g), 0.75 moles of unreacted Cl2(g) and 0.75 moles of H2O(g) at 800°C and 2 bar. Therefore recycling of unreacted steam or water and chlorine is required to reach the proposed output.

VOCl2 Reactor

This reaction is unique to this cycle. HSC-5 data show delta G is negative above 1207°C. HSC-5 equilibrium data show VOCl and VOCl3 in equal amounts and very little HCl(g) conversion below 2000°C. This reaction would be a candidate for an electrochemical reaction if there were sufficient solubility data for the solids and if significant formation of VOCl could be prevented. Therefore, this reaction is not technically feasible as proposed.

VOCl3 Reactor

This reaction is unique to this cycle. HSC-5 data show delta G does not approach zero at any temperature. HSC-5 equilibrium data also show no reaction. This reaction would be a candidate for an electrochemical reaction if there were sufficient solubility data for the solids and if significant formation of VOCl could be prevented. Therefore, this reaction is not technically feasible as proposed.

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PID 22 – IRON CHLORIDE-4

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Fe2O3-2	2Fe2O3 + 6Cl2(g) = 4FeCl3 + 3O2(g)	0.75	1000
Fe3O4	4Fe3O4 + O2(g) = 6Fe2O3	0.25	350
FeCl2-5	3FeCl2 + 4H2O = Fe3O4 + 6HCl + H2(g)	1	650
FeCl3-1	2FeCl3 = Cl2(g) + 2FeCl2	1.5	420
HCl-4	4HCl + O2(g) = 2Cl2(g) + 2H2O	1.5	400

SUMMARY

Using an electrochemical step for the FeCl2-5 reaction, and excess heat to generate steam for power production results in a calculated cycle efficiency of 36.6% at 50% source efficiency and 31.8% at 38% source efficiency. Therefore, further evaluation is not recommended.

DISCUSSION

It should be noted that complicated and expensive reactors and heat exchangers are required for these conditions to deal with high-temperature gases and the melting and boiling points of the reactants, such as:

Compound	MP	BP
FeCl2	677°C	1023°C
FeCl3	304°C	316°C

Fe2O3-2 Reactor

For this reaction, delta G < 0 above 1241°C and a temperature of at least 1300°C, where K = 2.27, is required for adequate kinetics. The solar duty at that temperature is 480 MJ/kg-mole of H2 produced, including 18 MJ of leak and an inlet/outlet counter-flow heat exchanger with 10°C minimum approach.

Fe3O4 Reactor

Delta G for this exothermic reaction is negative below 1361°C. Using minimum reactant temperatures, the reactor will operate at about 630°C with 5 MJ leak. This temperature is advantageous for feeding the Fe2O3 reactor heat exchanger.

FeCl2-5 Reactor

For this reaction, delta G < 0 only between 1023°C where FeCl2 is a gas and 1168°C, above which delta G is positive. The solar duty for this condition would be 601 MJ.

Using an electrochemical reactor eliminates the HCl(g) separation problem and the solar energy requirement by operating at 60°C, where the heat balance is neutral when the reactants are cooled and FeCl2(a) and water are fed at 60°C. Pressurized operation is required to deliver hydrogen at a useful pressure for distribution. Electrochemical operation will require 190 MJ in the reactor per kg-mole of H2 produced, resulting in 380 MJ of source energy at 50% source efficiency and 500 MJ at 38% source efficiency.

FeCl3-1 Reactor

Three FeCl cycles were originally proposed by Hardy-Grena, numbered MARK 7, 7a and 7b [1]. A problem was discovered in the FeCl3-1 decomposition reaction [2] that is common to the MARK 7, 7a, 7b (PID 22), MARK 9 (PID 4), MARK 14 and MARK 15 cycles. Delta G is negative for this exothermic reaction in three operating ranges: above 1403°C, between 677°C and 1023°C, and between 316 C and 572°C. This problem is illustrated by HSC-5 low-pressure equilibrium data, where a small peak in chlorine production is predicted just above the melting temperature of FeCl3 (304°C), and higher chlorine production does not occur below 1100°C. Operating in the low-temperature range allows about 240 MJ to be used to produce steam at about 300°C. Low-pressure operation requires a means to increase the pressure of the FeCl2 product for introduction to the FeCl2-5 reactor, unless that reactor is also operated at low pressure and a hydrogen compressor is used to provide pressurized hydrogen for distribution.

HCl-4 Reactor

Delta G for this exothermic reaction is negative below 595°C. Operation at 400°C, as proposed, provides adequate kinetics and allows about 110 MJ to be used to produce steam at about 390°C.

Steam Turbine Generator

Use of the excess heat from the FeCl3-1 and HCl-4 reactors in a steam turbine generator system, allows the production of about 50 MJ of electric power for the FeCl2-5 electrochemical reactor.

Correcting the phases required for these reactions and normalizing the multipliers results in the following table:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Fe2O3-2	3Fe2O3 + 9Cl2(g) = 6FeCl3(g) + 4.5O2(g)	0.5	1300
Fe3O4	2Fe3O4 + 0.5O2(g) = 3Fe2O3	0.5	630
FeCl2-5	6FeCl2(a) + 8H2O(l) = 2Fe3O4 + 12HCl(a) + 2H2(g)	0.5	60 (electrochemical)
FeCl3-1	6FeCl3(g) = 6FeCl2(s) + 3Cl2(g)	0.5	320
HCl-4	12HCl(g) + 3O2(g) = 6Cl2(g) + 6H2O(g)	0.5	400

Using an electrochemical step for the FeCl2-5 reaction, and excess heat to generate steam for power production results in a calculated cycle efficiency of 36.6% at 50% source efficiency and 31.8% at 38% source efficiency. Therefore, further evaluation is not recommended.

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PID 23 – MANGANESE CHLORIDE-1

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
MnCl2	3MnCl2 + 4H2O = Mn3O4 + 6HCl + H2(g)	1	700
HCl-6	4HCl + Mn3O4 = 2MnCl2 + MnO2 + 2H2O	1.5	100
MnO2-1	3MnO2 = Mn3O4 + O2(g)	0.5	900

Rewriting these reactions for whole number coefficients, showing appropriate phases and proposed operating temperatures follow:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
MnCl2	6MnCl2(ia) + 8H2O(l) = 2Mn3O4 + 12HCl(a) + 2H2(g)	0.5	60 (electrochemical)
HCl-6	12HCl(a) + 3Mn3O4 = 6MnCl2 + 3MnO2 + 6H2O	0.5	100
MnO2-1	3MnO2 = Mn3O4 + O2(g)	0.5	700

SUMMARY

The maximum thermal efficiency of the MARK 8 hybrid cycle is predicted to be about 31.4% for an electrical energy source efficiency of 50% and 23.8% for a source efficiency of 38%. Therefore, no further evaluation of this cycle is recommended.

DISCUSSION

MnCl2 Reactor

HSC-5 data show delta G = 0 at 1947°C for thermochemical reaction MnCl2. HSC-5 equilibrium data show very little H2(g) production below 2000°C at 50 bar. Therefore, an electrochemical step was investigated. At 60°C, 455 MJ of electrical energy is required. The source energy required is 1200 MJ at 38% source efficiency and 915 MJ at 50% source efficiency.

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PID 24 – HYBRID LITHIUM NITRATE

This hybrid process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
HI-1	2HI = I2(g) + H2(g)	1	300
I2-6	I2 + LiNO2 + H2O = 2HI + LiNO3	1	27 (electrochemical)
LiNO3	2LiNO3 = 2LiNO2 + O2(g)	0.5	427

Design of the reactors, separators and heat exchangers for this cycle depend on the melting and boiling points of the materials, as follows:

Compound	M.P., C	B.P., C
HI	-51	-35
I2	114	185
LiNO2	222	d. @ c 500
LiNO3	255	d. @ c 600

Inserting the correct phases for the proposed conditions results in the following table:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
HI-1	2HI(g) = I2(g) + H2(g)	1	300
I2-6	I2(a) + LiNO2(ia) + H2O(l) = 2HI(ia) + LiNO3(ia)	1	27 (electrochemical)
LiNO3	2LiNO3(g) = 2LiNO2(g) + O2(g)	0.5	427

SUMMARY

This hybrid cycle is not technically feasible if LiNO2 decomposes below 1200°C. If LiNO2 remains a gas at 1200°C, the LiNO3 reactor should operate there, and the thermal efficiency is 32.4% at an electrical source efficiency of 38% and 38.8% at an electrical source efficiency of 50%. Therefore, no further work on this cycle appears to be justified.

DISCUSSION

HI-1 System

This reaction is also used many other PIDs, including PIDs 1, 82 and 160, which were selected for assessment. HSC-5 data shows Delta G is slightly positive for all temperatures for this reaction, while K is slightly higher at higher temperatures. Fifty bar operating pressure is required to deliver pressurized hydrogen, and HSC-5 equilibrium data at 50 bar show about 0.17 moles of H2(g) and I2(g) generated at 300°C per mole of HI(g), with no change at lower pressures. This requires separation and recycle of unreacted HI within a system that contains a distillation column operating at 20 bar, as shown in Fig. 2 of Ref. [1]. The solar energy requirement for this system is 177 MJ per kg-mole of H2 produced.

I2-6 Reactor

This electrochemical reaction is unique to this cycle. This reactor can be operated at low pressure and HI(ia) pumped to 20 bar for introduction to the HI-1 system. HSC-5 data show that delta G is 148 at 30°C for this reaction. Total voltage required is –1.2 V for delivering 230 MJ to the reactor. For a source efficiency of 38%, 604 MJ must be expended, while a source efficiency of 50% requires 460 MJ per kg-mole of H2 produced.

LiNO3 Reactor

This reaction is unique to this cycle. HSC-5 data show that delta G is negative above 940°C for this reaction, with K about 43 at 1200°C. HSC-5 equilibrium data show that about 0.1 moles of LiNO3 remain at 1200°C and 2 bar. Operation at 50 bar shifts the temperature at which 0.1 bar of LiNO3 remains above 1500°C. **If LiNO2 decomposes at 500°C, this reaction is not technically feasible.** If this reaction is technically feasible at 1200°C, a counter-flow input-output heat exchanger would reduce the solar energy required to 130 MJ plus heat leak.

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[1]   H. Engels, K. Knoche, M. Roth, "Direct Dissociation of Hydrogen Iodide – an Alternative to the General Atomic Proposal," *Int. J. Hydrogen Energy,* Vol. **12**, No. 10, pp. 675-678. 1987.

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[3]   Y. Shindo, K. Ito, K. Haraya, T. Hatuka, H. Yoshitome, "Kinetics of the Catalytic Decomposition of Hydrogen Iodide in the Thermochemical Hydrogen Production," *Int. J. Hydrogen Energy,* Vol. **9**, No. 8, pp. 695-700. 1984.

[4]   M. Christahl, U. Arnold, "Liberation of hydrogen Iodide from Aqueous Solutions with Lithium Iodide," *Int. J. Hydrogen Energy,* Vol. **8**, No. 8, pp. 597-601. 1983.

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PID 25 –CESIUM HYDROXIDE

This cycle is based on the following chemical reactions from Ref. [1]:

Reaction No.	Reaction Code	Formula	Multiplier	Max. Temp. (°C)
25A	Cs	$2Cs + 2H_2O = 2CsOH + H_2(g)$	1	450
25B	Cs2O	$2Cs_2O = 4Cs + O_2(g)$	0.5	2700
25C	CsO2	$4CsO_2(s) = 2Cs_2O(s) + 3O_2(g)$	0.5	450
25D	CsOH-1	$4CsOH + 3O_2(g) = 4CsO_2 + 2H_2O$	0.5	250

SUMMARY

Reaction 25B, the thermal decomposition of Cs2O, is nonspontaneous at temperatures between zero and 2721°C (2994 K). Reaction 25D is nonspontaneous at temperatures from 0 to 3000°C. Because only reactions at temperatures ≤2200°C are considered viable for solar heaters in these evaluations, PID 25 is not workable and further evaluation of this cycle is unnecessary.

REACTION 25A

Calculations using HSC 5 (Ref. [2]) show that reaction 25A is spontaneous at temperatures from 0 to 2713°C, thus indicating that the 450°C specified temperature is excessive. This exothermic reaction should be run in aqueous solution at 25°C to facilitate heat removal and separation of H2 from H2O.

REACTION 25B

Reaction 25B, the thermal decomposition of Cs2O, is nonspontaneous at temperatures between zero and 2721°C (2994 K) where delta G is zero (Ref. [2]). Because only reactions at temperatures ≤2200°C are considered viable for solar heaters in these evaluations, PID 25 is not workable and further evaluation of this cycle is unnecessary.

REACTION 25C

Reaction 25C is spontaneous above 1258°C where delta G = 0. This indicates that the specified 450°C temperature is too low and would require revision if this were a viable cycle.

REACTION 25D

Reaction 25D is nonspontaneous at temperatures from 0 to 3000°C. This is further indication that PID 25 is nonworkable as presented in Ref. [1].

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

 [2]   Computer program, "Outokumpu HSC Chemistry for Windows", Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

PID 26 – COPPER MAGNESIUM CHLORIDE

This cycle is based on the following chemical reactions as specified in Refs. [1,2]:

Reaction No.	Formula	Multiplier	Max. Temp. ($^{\circ}$C)
26A	$2Cl2(g) + 2Mg(OH)2(s) = 2MgCl2(s) + 2H2O(l) + O2(g)$	0.50	25
26B	$2Cu (s) + 2HCl (g) = 2CuCl (s)+ H2(g)$	1.00	100
26C	$2CuCl (s) = Cu (s)+ CuCl2 (s)$	2.00	100
26D	$2CuCl2(s) = 2CuCl (l)+ Cl2(g)$	1.00	500
26E	$MgCl2 (s) + 2H2O (g) = 2HCl (g) + Mg(OH)2 (l)$	1.00	450

SUMMARY

Total calculated solar heat input to the process is 1385 MJ. Seventy percent of this heat is needed in the 26C1 evaporator to separate the water of dissolution from the CuCl2 product. **This requirement drives the overall efficiency of the cycle down to 20.6%. This is sufficiently low to preclude a further evaluation of the cycle.**

It should be noted that PID 26 is similar to PID 39 and PID 56 (Ref. [1]) that are being assessed by others in this program. Reference [4] presents a hybrid thermochemical-electrolysis water splitting cycle that requires only the reactions used in 26B, 26C1 and 26D1. Reference [5] also presents a study of a 4-step copper-chlorine thermochemical cycle with one electrochemical reaction. The calculated heat-to-hydrogen efficiency of the Ref. [5] cycle is 41%.

Discussions of each reaction along with a simplified flowsheet for this cycle (Fig. 1) are shown below.

REACTION 26A

Calculations made with Ref. [3] show that reaction 26A, as presented above with liquid H2O product, must be operated at temperatures above 540°C where delta G is zero. If the H2O is allowed to vaporize however, the reaction will proceed at temperatures ≥133°C (see Reaction 26A1 below).

REACTION 26B

Reaction 26B will proceed as specified above and in Ref. [1].
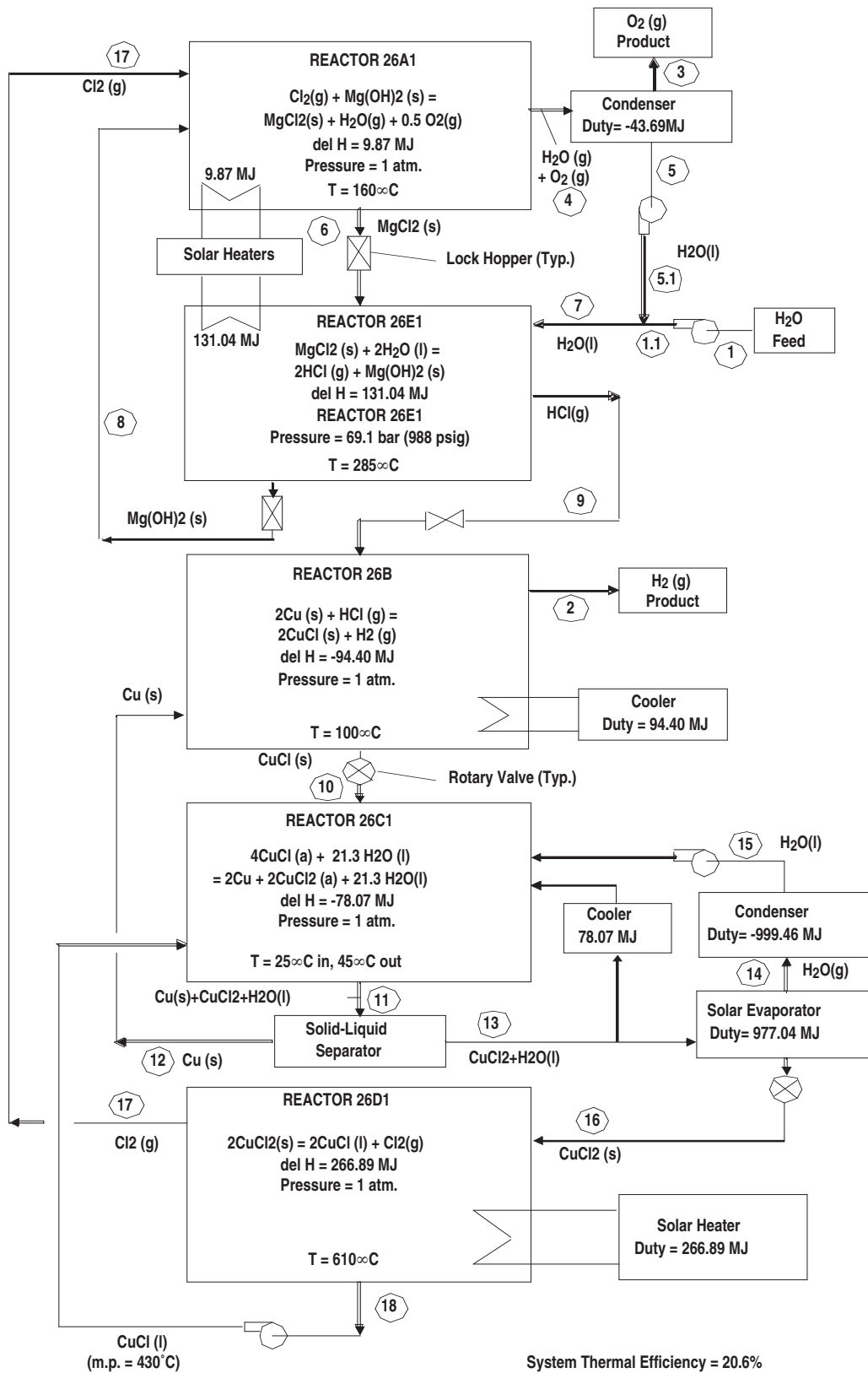
Fig. 1. Solar hydrogen generation project PID 26 flowsheet, Rev. 1.

A2-38

REACTION 26C

Reaction 26C, as specified above, does not produce a temperature below 5000°C at which delta G is zero. Yet, if this Reaction is performed in an aqueous solution, it will proceed at temperatures ≤51°C as shown in Reaction 26C1 below. The two moles of CuCl2 product require 21.3 moles water for dissolution. After separation of the Cu product, the water must be evaporated from the CuCl2 to preclude the Cl2 + H2O reaction in reactor 26D1.

REACTION 26D

Reference [3] calculations indicate that Reaction 26D is nonspontaneous at the specified temperature of 500°C. The reaction will proceed however, if the temperature is increased to ≥589°C (see Reaction 26D1 below).

REACTION 26E

Reaction 26E will not work as proposed above with steam as a reactant. If the pressure is increased to >59.4 bar (847 psig) so that the water remains liquid at 275°C, the reaction will proceed in the aqueous solution (see Reaction 26E1 below). The pressure at the proposed operating temperature of 285°C is 69.1 bar (988 psig). Note also that the Mg(OH)2 does not melt at this temperature.

The cycle, with these modifications, becomes PID 26.1 with the following reactions:

Reaction No.	Formula	Multiplier	Max. Temp. (°C)
26A1	2Cl2(g) + 2Mg(OH)2(s) = 2MgCl2(s) + 2H2O(g) + O2(g)	0.50	160
26B	2Cu (s) + 2HCl (g) = 2CuCl (s)+ H2(g)	1.00	100
26C1	2CuCl (a) = Cu + CuCl2 (a)	2.00	25 to 45
26D1	2CuCl2(s) = 2CuCl (l)+ Cl2(g)	1.00	610
26E1	MgCl2 (s) + 2H2O (l) = 2HCl (g) + Mg(OH)2 (s)	1.00	285

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   L.O. Williams, "Hydrogen Power: An Introduction to Hydrogen Energy and Its Applications," Pergamon Press, 1980 pp 158(t).

[3]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

[4] M. Dokiya and Y. Kotera, "Hybrid Cycle with Electrolysis Using Cu-Cl System," International Journal of Hydrogen Energy, Vol. **1**, pp 117-121, 1975.

[5] Michele Lewis, "Low-Temperature Thermochemical Generation of Hydrogen from Water", Argonne National Laboratory website http://www.cmt.anl.gov/science-technology/lowtempthermochemical.shtml.

PID 36 –CESIUM AMALGAM-1

This process is based on the following chemical reactions as specified in Refs. [1,2]:

Reaction No.	Reaction Code	Formula	Multiplier	Max. Temp. (°C)
36A	CsOH	$2CsOH(l) = Cs_2O(s) + H_2O(g)$	1.0	410
36B	Cs2Hg	$2HgO(l) = 2Hg(g) + O_2(g)$	0.5	500
36C	Cs2O-1	$Cs_2Hg + 2H_2O(g) = 2CsOH(l) + Hg(g) + H_2(g)$	1.0	600
36D	HgO	$Cs_2O(s) + 2Hg(l) = Cs_2Hg + HgO(s)$	1.0	300

SUMMARY

Because the required temperatures for Reaction 36A cannot economically be reached in solar heaters, this cycle is unworkable for this assessment.

Discussions of each reaction are shown below.

REACTION 36A

Calculations using HSC 5 (Ref. [3]) show that reaction 36A, the thermal decomposition of CsOH, is nonspontaneous at temperatures below 3170°C (3443 K) where delta G is zero. Thermal decomposition of NaOH, a similar compound that could possibly be substituted for CsOH, showed a positive delta G for all temperatures below 2730°C (3003 K). Because the required temperatures cannot economically be reached in solar heaters, this cycle is unworkable for this assessment.

REACTION 36B

The 500°C temperature specified for reaction 36B is too low. Delta G = 0 at 584°C for HgO decomposition, so the reactor operating temperature should be increased to 600°C.

REACTION 36C

The Cs component of reaction 36C is spontaneous at temperatures below 2290°C. If it is necessary to vaporize the Hg (b.p. Hg = 357°C), the specified 600°C temperature is excessive and can be lowered to 380 to 420°C. If laboratory tests show that the Hg can remain liquid for the cycle, ambient temperature should be adequate for this reaction.

REACTION 36D

HSC 5 will evaluate individual components of an amalgam as in reaction 36C, but it will not show a result for an amalgam as a reaction product such as the Cs2Hg in 36D. This reaction, therefore, was not evaluated.

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   l.O. Williams, "Hydrogen Power: An Introduction to Hydrogen Energy and Its Applications", Pergamon Press, 1980 pp 158(t).

[3]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

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PID 49 –URANIUM CARBONATE-1

This process is based on the following chemical reactions from Ref. [1]:

Reaction No.	Reaction Code	Formula	Multiplier	Max. Temp. (°C)
49A	CO2-4	$3CO_2 + U_3O_8 + H_2O = 3UO_2CO_3 + H_2(g)$	1.0	25
49B	UO2CO3	$3UO_2CO_3 = 3CO_2(g) + 3UO_3$	1.0	250
49C	UO3	$6UO_3(s) = 2U_3O_8(s) + O_2(g)$	0.5	700

SUMMARY

Calculations using Ref. [3] show that reaction 49A is non-spontaneous at temperatures between 0 and 3000°C. This indicates that PID 49 is not workable, and further evaluation of this cycle is unnecessary.

Attempts to modify the cycle PID 49 by adding Na_2CO_3 or $(NH_4)_2CO_3$ salts to introduce CO_2 into reaction 49A to react with the U_3O_8 were unsuccessful.

Discussions of each reaction are shown below.

REACTION 49A

Calculations using Ref. [3] show that reaction 49A is nonspontaneous at temperatures between 0 and 3000°C. This indicates that PID 49 is not workable, and further evaluation of this cycle is unnecessary.

REACTION 49B

Reference [3] data for Reaction 49B show that this reaction is spontaneous at temperatures above 158°C, where delta G is zero.

REACTION 49C

Reaction 49C is spontaneous at temperatures above 672°C, where delta G is zero.

REFERENCES

[1] UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2] L.O. Williams, "Hydrogen Power: An Introduction to Hydrogen Energy and Its Applications," Pergamon Press, 1980 pp 158(t).

[3]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

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PID 50 –LITHIUM MANGANESE

This cycle is based on the following chemical reactions from Ref. [1]:

Reaction No.	Formula	Max. Temp. (°C)
50A	$3Mn_2O_3 = 2Mn_3O_4 + 0.5\ O_2(g)$	977
50B	$6LiOH + 2Mn_3O_4 = 3Li_2O.Mn_2O_3 + H_2(g) + 2H_2O$	700
50C	$3Li_2O.Mn_2O_3 + 3H_2O = 6LiOH + 3Mn_2O_3$	80

SUMMARY

A search of compounds in the Ref. [2] database did not locate $Li_2O.Mn_2O_3$ (specified as a product of reaction 50B and a reactant in reaction 50C), or any similar species containing Li and Mn. Equilibrium calculations using only the constituents Li_2O and Mn_2O_3 (but not the specified compound) indicate that H_2 is not produced by reaction 50B (Reaction Code LiOH).

Reaction 50B was also entered into the Equili-web database (http://www.crct.polymtl.ca/ equiweb.php) for 500, 700, 1000, 1200, 1500, 2000, and 2200°C equilibrium temperatures. The resulting maximum hydrogen production for this reaction was 0.10396E-02 mole H_2 and 0.71578E-03 mole H at 2200°C. **This low yield indicates that PID 50 is not a viable candidate for commercial hydrogen production.**

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

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PID 51 – POTASSIUM PEROXIDE

This process is based on the following proposed chemical reactions from the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
K	2K + 2KOH = 2K2O + H2(g)	1	725
K2O	2K2O = 2K + K2O2	1	825
K2O2	2K2O2 + 2H2O = 4KOH + O2	0.5	125

SUMMARY

Therefore, the PID 51 Gaz de France cycle does not work as proposed, and does not warrant further development.

DISCUSSION

The reactions are unique to the proposed cycle. The cycle is reported to us as thermochemical.

Related phase data for the solids are shown in the following table:

Compound	M.P. C	B.P. C
K	64	759
KOH	406	1323
K2O	878	?
K2O2	490	?

K Reactor

HSC-5 data show that the proposed endothermic K reaction does not have a temperature at which delta G = 0. The figure below shows KOH & K are stable up to about 750°C, at which point K(g) is evolved. Thermally, H2 is only evolved well above 2500°C.

Perhaps the reaction was proposed as an electrolysis in molten KOH-we do not have the reference.

K2O Reactor

HSC-5 data for the proposed endothermic K2O reaction show that delta G is negative only above 1923°C where all of the compounds are gases, and for no other phases or temperatures. If the K2O feed can be heated and melted to 900°C by cooling and condensing reactor products, the calculated solar heat requirement is 724 MJ per kg-mole of H2 produced plus heat leak.

K2O2 Reactor

HSC-5 data for the proposed exothermic K2O2 reaction show that delta G is negative for all temperatures and phases. If the K and K2O2 reactions are both aqueous, the KOH(a) can be pumped from one vessel to the other without drying. This approach requires the rejection of 305 MJ of heat from the K2O2 reactor.

Ignoring any energy cost for electrolysis in the first reaction, the efficiency of this cycle is 27.8%. Thus as a hybrid, the efficiency is less than 27%. As a thermochemical cycle, the efficiency is zero.
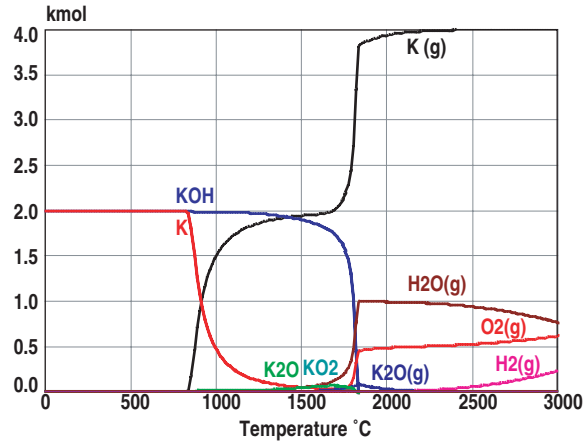
PID 53 –HYBRID CHLORINE

This process is based on the following chemical reactions:

Reaction Code	Formula	Multiplier	Max. Temp. (°C)
Reverse Deacon	$2Cl2(g) + 2H2O(g) = 4HCl(g) + O2(g)$	0.5	800
Uhde	$2HCl(a) = Cl2(g) + H2(g)$	1	80

SUMMARY

The overall efficiency of this cycle is 25.5%

DISCUSSION

Thermochemical processing of HCl is energy-intensive, since it requires high temperature operation and has relatively low single-pass conversions. Until recently, the only available electrolytic process for chlorine was the Uhde process, operating at 70–90°C. The feed to the Uhde process is 22 wt% hydrochloric acid and the chlorine is typically produced with 1-2 wt% water vapor [1]. Recently, Dupont has developed an electrolytic process that produces dry chlorine for industrial use at 450-550 kPa (4.5-5.5 bar), but requires an extensive drying train. Since water is required for feed to the reverse Deacon reaction in the PID 53 process, the Udhe system was selected for evaluation at 80°C and 5 bar. The electrolyzer requires 343 MJ/kg of H2 for electrolysis reactions. An assumed operating efficiency of 88% results in an electric power requirement of 390 MJ/kg of H2.

In the flowsheet (Fig. 1) shown with the mass balance (Table 1), chlorine is produced at the electrolyzer anode and flows to an inline mixer with a small amount of water vapor, where it is mixed with water from the electrolyzer. Hydrogen is produced at the cathode and washed before being removed for beneficial use at about 4.5 bar pressure. The mixture of chlorine and water is introduced to a solar heater operating at about 800°C, where one mole of H2O(g) reacts with one mole of Cl2(g) to produce 2 moles of HCl(g) and on-half mole of oxygen via the reverse Deacon reaction [2]. Excess water from the electrolyzer feed is recirculated in this system.

The hot gas from the solar heater can be used to directly produce electric power for the electrolyzer through an expander; however, there is insufficient pressure and flow to meet this requirement. Therefore, a more conventional heat recovery boiler (HRB) and steam turbine generator operating at 100 bar was selected for evaluation. The HRB can reduce the temperature of the offgas sufficiently to condense all of the excess water at the temperature required by the electrolyzer and for separation of washed oxygen.

Fig. 1. PID 53 flowsheet.
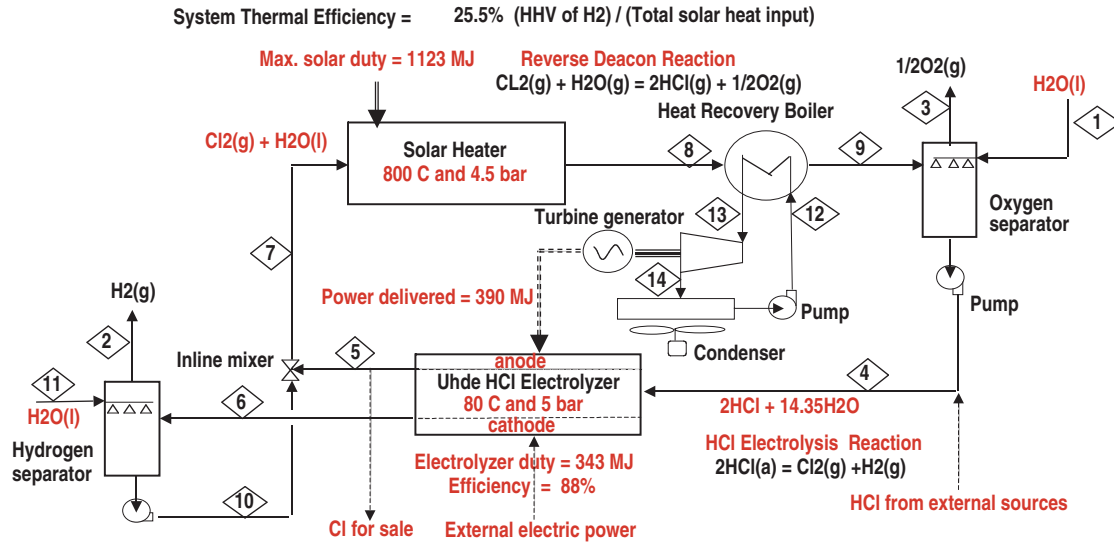
The steam turbine generator can produce sufficient power (390 MJ/kg of H2) for the electrolyzer with a vacuum condenser operating at 0.3 bar absolute and discharging condensate to the HRB via a boiler feed pump. Emissions and effluents from the cycle can be eliminated in this approach.

The solar heater duty required is 1123 MJ/kg of H2, resulting in an overall efficiency of 25.5%. The proposed system can be sized to produce excess 22-wt% hydrochloric acid during periods of high solar incidence. The excess acid could be electrolyzed during off-peak incidence using externally generated power to produce hydrogen full-time.

In addition, waste HCl could be used with external power during off-peak solar periods to produce both hydrogen and recycled chlorine, as proposed by Dupont [1]. For external power generated at an efficiency of 35%, the overall efficiency of the system would remain at about 26%.

REFERENCES

[1]   S. Motupally, D. Mah, F. Friere, J. Weidner, "Recycling Chlorine from Hydrogen Chloride," *The Electrochemical Society* **Interface**, pp. 32-36. Fall 1998.

[2]   A. Gupta, R. Parker, C. Keefer, R. Hanrahan, "Gas Phase Formation of Hydrogen Chloride by a Solar-Driven Chlorine-Steam Reaction," *Int. J. Hydrogen Energy,* Vol. **17**, No. 10, pp. 757-762. 1992.

TABLE 1. PID 53 Mass Balance

PID 53 - Hallett Air Products

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Description	Water	Hydrogen	Oxygen	Hydrochloric acid to electrolyzer	Cl(g) + H2O(l) from electrolyzer	H2 to separator	Cl(g) + H2O(l) to solar heater	HCl(g) + O2(g) from solar heater	HCl(l) + H2O + O2 from HRB	Water from H2 separator	Water to H2 separator	Water to HRB	Steam from HRB	Steam from turbine
Temperature, C	25	25	25	80	80	80	79	800	85	56	25	60	600	70
Pressure (absolute), bar	10	4.5	3.5	5	5	5	5	4.5	4	5	10	101	100	0.312
Volume, normal cu. m.	0.01	22.91	11.40	0.26	22.79	23.17	23.06	371.23	11.65	0.27	0.01	0.34		
Volume, actual cu. m. (GPM)	0.01	5.46	3.49	0.26	5.79	5.88	5.66	318.41	3.68	0.27	0.01	0.34	13.06	1.96
Gases														
Cl2(g)					70.91		70.91							
H2(g)		2.02				2.02								
HCl(g)								72.92						
H2O(g)								252.59					340.00	289.00
O2(g)			16.00					16.00	16.00					
Total gases	0.00	2.02	16.00	0.00	70.91	2.02	70.91	341.51	16.00	0.00	0.00	0.00	340.00	289.00
Liquids & Solutions														
HCl(a)				72.92					72.92					
H2Ol(l)	5.94			258.54		258.54	270.61		252.59	270.61	12.07	340.00		51.00
Total liquids/solutions	5.94	0.00	0.00	331.46	0.00	258.54	270.61	0.00	325.52	270.61	12.07	340.00	0.00	51.00
Solids														
Total solids	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total gases, liquids & solids	5.94	2.02	16.00	331.46	70.91	260.55	341.51	341.51	341.51	270.61	12.07	340.00	340.00	340.00

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PID 56 – Copper Chloride

This hybrid cycle is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (°C)
Cl2-1	2Cl2(g) + 2H2O(g) = 4HCl(g) + O2(g)	0.5	800
CuCl2	2CuCl2 = 2CuCl + Cl2(g)	1	500
CuCl-2	2CuCl + 2HCl = 2CuCl2 + H2(g)	1	200

SUMMARY

The resulting efficiency, including the electrical input for the electrochemical CuCl-2 reaction step, is 31.2% at a source efficiency of 38% and 34.5% at a source efficiency of 50%. Therefore, further evaluation is not recommended.

DISCUSSION

Design of the reactors, separators and heat exchangers for this cycle depend on the solubility, melting and boiling points of the materials from the CRC and HSC-5, as follows:

Compound	M.P., C	B.P., C	Solubility
CuCl	430	1400	Soluble in HCL(a)
CuCl2	598	827	Soluble

Inserting the correct reactions, phases and multipliers for the required conditions explained below results in the following table:

Reaction Code	Formula	Multiplier	Max. Temp. (°C)
Cl2-1	2Cl2(g) + 2H2O(g) = 4HCl(g) + O2(g)	0.5	620
CuCl2	2CuCl2(l) = 2CuCl(l) + Cl2(g)	1	730
CuCl-2	2CuCl(a) + 2HCl(a) = 2CuCl2(a) + H2(g)	1	60 (electrochemical)

Cl2-1 Reactor

This reaction is also used in many other PIDs, including 16, 53, 103 and 195, which have been selected for assessment. HSC-5 data for this reaction show that delta G is negative above 595°C. HSC-5 equilibrium data show that about 0.67 moles of HCl(g), 0.167 moles of O2(g),

0.67 moles Cl2(g) and 0.67 moles of H2O(g) are produced in the reactor effluent at 620°C and 20 bar for each mole of H2O(g) and HCl(g) introduced to the Cl2-1 reactor. A recycle rate of twice the feed rate is required to produce two moles of HCl(g) and 0.5 moles of O2(g). A counter-flow inlet-outlet heat exchanger can increase the feed temperature to the reactor to 520°C and reduce the solar heat requirement to 82 MJ per kg-mole of H2 produced, while providing pre-cooling for separation of O2(g), HCl(a) and Cl2(g). A membrane separator is required for Cl2(g) and O2(g).

CuCl2 Reactor

This reaction is also used in several other PIDs, including PID 26, which was selected for assessment. HSC-5 data for this reaction show that delta G is negative above 598 C. HSC-5 equilibrium data show that about one mole of CuCl(l), one mole of CuCl2(l) and 0.5 moles Cl2(g) are produced in the reactor effluent at 730°C and 20 bar for two moles of CuCl2(s) introduced to the CuCl2 reactor. A recycle rate equal to the feed rate is required to produce two moles of CuCl(l) and one mole of Cl2(g). A counter-flow inlet-outlet heat exchanger can increase the feed temperature to the reactor to 580°C and reduce the solar heat requirement to 462 MJ per kg-mole of H2 produced, while providing pre-cooling for separation of Cl2(g), H2O(l), CuCl(s) and CuCl2(a).

CuCl-2 Reactor

Delta G for the CuCl-2 reaction is positive at all temperatures, so an electrochemical step is proposed. This approach requires CuCl(aq), which is facilitated but the solubility of CuCl in HCl(a) in water at 60°C. A membrane is required to separate unreacted CuCl solution from CuCl2 solution for discharge. A Pourbaix diagram shows a very limited region of pH from -1 to +4 where CuCl2 is stable in an electrochemical environment [1]. The electrical energy requirement is 60 kJ at 60°C, and the source energy requirement is 284 MJ at 50% source efficiency and 373 MJ at 38% source efficiency.

The resulting efficiency, including the electrical input for the electrochemical CuCl-2 reaction step, is 31.2% at a source efficiency of 38% and 34.5% at a source efficiency of 50%. Therefore, further evaluation is not recommended.

REFERENCES

[1]   D. Scott, "The Reactions of Cuprous Chloride,"
        http://aic.stanford.edu/jaic/articles/jaic29-02-007_3.html.

PID 61 – SODIUM-IRON

This process is based on the following chemical reactions [1]:

Reaction Code	Formula	Multiplier	Proposed Temp. (°C)
Fe2O3-3	$6Fe_2O_3 = 4Fe_3O_4 + O_2(g)$	0.5	1470
Fe3O4-2	$2Fe_3O_4 + 6NaOH(a) = 3Na_2O.Fe_2O_3 + 2H_2O(l) + H_2(g)$	1.0	1140
Na2O-2	$3Na_2O.Fe_2O_3 + 3H_2O(l) = 3Fe_2O_3 + 6NaOH(a)$	1	530

Reaction Fe2O3-3 Evaluation

The equilibrium composition for the reduction of hematite over temperatures ranging from 100°C to 1600°C is shown in Fig. 1.
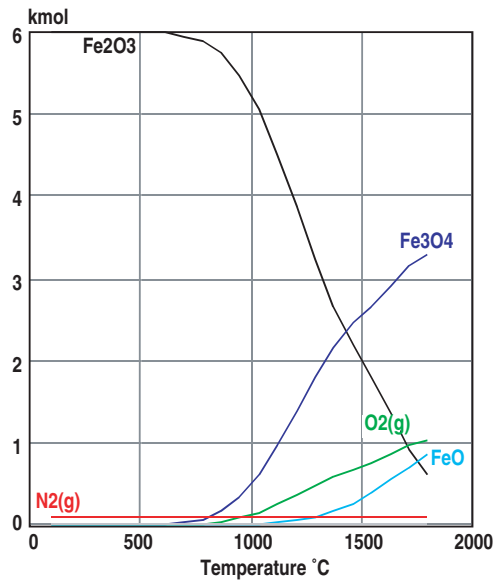
Fig. 1. Reduction of hematite.

The oxygen production at 1470°C is about 0.7 mol, which is somewhat less than the stoichiometric amount. In addition, some of the hematite forms wustite, which is a liquid above 1377°C. The wustite is capable of producing hydrogen in the presence of sodium hydroxide at temperatures in excess of 400°C, so it is not parasitic.

Reaction Fe3O4-2 Evaluation

The equilibrium composition of the reaction products for the oxidation of magnetite in sodium hydroxide is shown in Fig. 2.
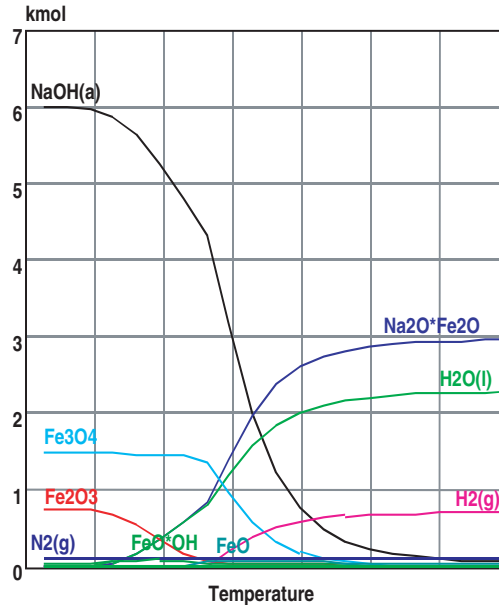
Fig. 2. Magnetite oxidation in sodium hydroxide.

Hydrogen production is near a maximum at around 500°C. For this reason, the reaction temperature for magnetite oxidation should be changed from the original proposed temperature of 1140 C to 500°C (if the kinetics allow). It should be noted that for this analysis the system is assumed to be at a pressure of 1 bar. It may be necessary to run at an elevated pressure to prevent evaporation, depending on the sodium hydroxide solution concentration and reaction temperature. Running at elevated pressure could reduce the amount of hydrogen produced by shifting the equilibrium to the left.

Reaction Na2O-2 Evaluation

The equilibrium composition of the products of the reaction of sodium ferrite and water at 50°C is shown in Fig. 3.

This reaction goes to completion at temperatures less than 100 C, but may have slow kinetics.
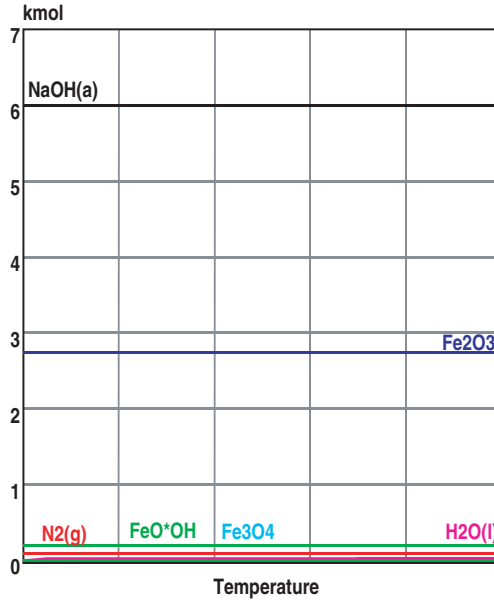
Fig. 3. Sodium ferrite decomposition.

Hydrogen production

The viability of the process as a whole is a function of the amount of hydrogen produced as well as the implementation and efficiency of each of the three steps. The amount of hydrogen production can be evaluated by performing an iterative equilibrium analysis. This involves taking the output composition of one reaction and inputting it to the next; eventually, the composition converges to a steady state value and the amount of hydrogen production can be determined. The extent of reaction (EOR), which is a measure of hydrogen conversion efficiency, is defined as the amount of hydrogen produced at steady state divided by the stoichiometric amount, as shown in Eq. (1).

$$EOR = \frac{mol_{H_2 \, SS}}{mol_{H_2 Stoich}} \tag{1}$$

The extent of reaction calculated based on the equilibrium composition is 0.69, indicating that the amount of hydrogen produced is about 70% of the maximum possible amount for this process.

Another measure of the hydrogen production efficiency is the ratio of the amount of hydrogen produced to the amount of metal oxide input to the high temperature reduction step. For this process, 0.23 moles of hydrogen are produced for every mole of hematite (0.33 molH2/molFe2O3 is the maximum possible for the process). This number is helpful in that it allows this process to be compared with others. For instance, the two step magnetite/wustite process can produce a maximum of 1 molH2/molFe3O4.

Process Implementation

For this analysis, the three steps are assumed to occur as described below.

Fe2O3-3: Solid hematite is input to the high temperature reduction reactor along with heat from a solar source. Magnetite is formed as a solid at 1470°C along with oxygen gas at a partial pressure less than 1 atm. An inert gas is used to remove the oxygen from the reactor in order to prevent the back reaction upon cooling of the magnetite. It may be possible to transfer heat from the magnetite exiting the reactor to the hematite entering the reactor. This recuperation is more than likely a necessity given the relatively low hydrogen yield (molH2/molFe2O3).

Fe3O4-2: Solid magnetite is reacted with aqueous sodium hydroxide at 500°C. This step will require pressurization given that concentrated sodium hydroxide solutions have a maximum boiling point of about 350°C [2]. Hydrogen gas is produced and removed from the reactor. The sodium ferrite product is transferred to another reactor and cooled.

Na2O-2: Liquid water is added to sodium ferrite at 50°C. Solid hematite and aqueous sodium hydroxide are produced. The hematite is transferred to the high temperature reactor, receiving thermal energy via recuperation along the way. Aqueous sodium hydroxide is pumped to the Fe3O3-2 reactor, also receiving thermal energy via recuperation.

The process diagram, Fig. 4, shows all of the system components as well as mass and energy flows.
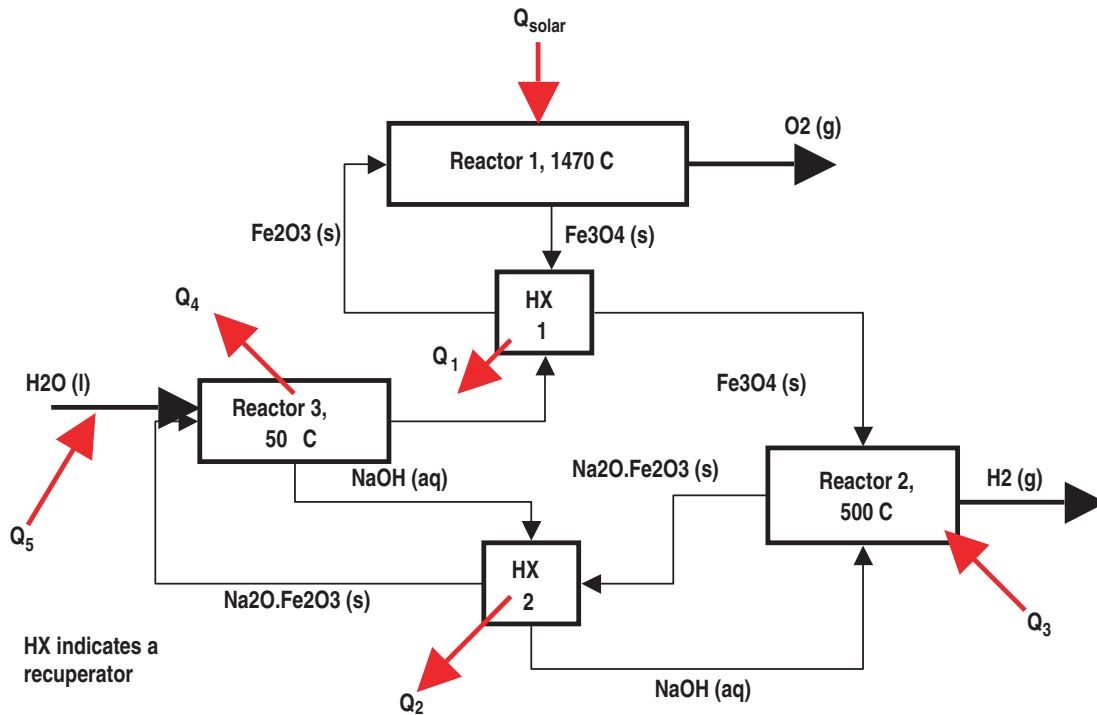
Fig. 4. Process diagram.

Table 1 is a listing of the principle energy inputs and outputs for the process. High and low process efficiency is calculated from these results. The high efficiency corresponds to optimum heat recuperation. The low efficiency corresponds to operation without heat recuperation. In both cases, efficiency is defined as the HHV of the hydrogen produced divided by the required process heat input.

Table 1. Principle energy flows

Step	Heat input, MJ
Reaction Fe2O3-3 at 1470 C, Q_{solar}	166
Cooling of reduced products (magnetite) from 1470 C to 500 C, Q_1	-435
Reaction Fe3O4-2 at 500 C, Q_3	385
Cooling of sodium ferrite from 500 C to 50 C, Q_2	-398
Reaction Na2O-2, Q_4	-244
Heating of oxides (hematite) from 50 C to 1470 C, Q_1	625
Heating of NaOH from 50 C to 500 C, Q_2	101
Heating of water from 25 C to 50 C, Q_5	5.7

The HHV of hydrogen at STP is 286 MJ/kmol. For this process, 0.689 kmol of hydrogen is produced which amounts to 197 MJ of chemical energy. Assuming no recuperation of thermal energy, the system heat requirement is 1283 MJ. The process efficiency in this case is 15%. Recuperation may be used to preheat the hematite upstream of the high temperature reduction step (Fe2O3-3) by transferring heat from the magnetite exiting the reaction at 1470 K. A total of 435 MJ can be recuperated here. In addition, the sodium hydroxide can be preheated from 50°C to 500°C by receiving heat from the sodium ferrite product of the Fe3O4-2 reaction. This allows for the recuperation of 101 MJ. It is unlikely that the product heat of reaction Na2O-2 can be used since it is produced at 50°C. With recuperation, the energy requirements of the process can be reduced to 747 MJ, resulting in a process efficiency of 27%.

CONCLUSION

An efficiency of 27% is too low for a practical hydrogen production process. There is little that can be done to improve the efficiency of this process because the principal inefficiency is in the chemistry. Production of 1/3 mol of hydrogen for every mole of Fe2O3 (maximum) just isn't good enough. In addition, the temperature of the hematite reduction step (1470°C) puts this process just out of the range of what proven power tower technology can do. Dish concentrators are capable of achieving the required temperatures, but they are unsuited to processes involving aqueous solutions.

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[1]   S. Yalcin, "A Review of Nuclear Hydrogen Production," *Int*. *J. Hydrogen Energy,* Vol. **14**, No. 8, pp. 551-561.

[2]   Perry and Chilton "Chemical Engineers Handbook," *McGraw-Hill,* 1973, p. 368.

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PID 62 – IRON BROMIDE

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Br2-1	2Br2 + 2H2O = 4HBr + O2(g)	0.5	1000
Fe3O4-4	Fe3O4 + 8HBr = Br2 + 3FeBr2 + 4H2O	1	300
FeBr2	3FeBr2 + 4H2O = Fe3O4 + 6HBr + H2(g)	1	600

SUMMARY

The cycle as proposed has several thermodynamic difficulties, which would imply an efficiency of zero.

If a 2,000°C solar source is available, the total solar duty of this hybrid cycle is 872 MJ per kg-mole of H2 produced. Therefore, the efficiency is 32.8%, not including a thermochemical step for the FeBr2 reaction, and this cycle should not be considered for further development.

DISCUSSION

Br2-1 Reactor

This reaction is unique to this cycle. HSC-5 data for the Br2-1 reaction show that delta G is negative only above 1874°C and a temperature of 2000°C is necessary for adequate kinetics. A counter-flow input/output heat exchanger limits solar duty to 214 MJ per kg-mole of H2 produced plus heat leak for this reactor.

Fe3O4 Reactor

This reaction is also proposed for PID 72. HSC-5 data for the Fe3O4-4 reaction show that delta G is negative below 619°C. Since the HBr feed must be condensed to separate oxygen, a counter-flow heat exchanger will not save any heat, and the solar energy requirement for this reactor is 658 MJ per kg-mole of H2 produced plus heat leak for this reactor.

FeBr2 Reactor

This reaction is also proposed for PID 72, as well as PID 139. HSC-5 data for the FeBr2 reaction show that delta G is negative only above 1399°C. Since FeBr2 and HBr are soluble, this reaction may be a good candidate for an electrochemical reactor operating at 100°C.

Modifying the chemical reaction table to match the required conditions results in the following table:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Br2-1	2Br2(g) + 2H2O(g) = 4HBr(g) + O2(g)	0.5	2000
Fe3O4-4	Fe3O4 + 8HBr(ia) = Br2(g) + 3FeBr2 + 4H2O(g)	1	300
FeBr2	3FeBr2(ia) + 4H2O(l) = Fe3O4 + 6HBr(ia) + H2(g)	1	100 (electrochemical

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PID 63 – Iron-Carbon Monoxide-2

The Euratom 1970 De Beni cycle is based on the following two reactions from Ref. [1].

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
C	C(s) + H2O(g) = CO(g) + H2(g	1	700
CO	CO(g) + 2Fe3O4(s) = C(s) + 3Fe2O3(s)	1	250
Fe2O3-3	6Fe2O3 = 4Fe3O4 + O2(g)	0.5	1470

Calculations using HSC, Ref. [2], indicate negative delta G at the temperatures indicated for all three reactions. However, for the second reaction (CO(g) + 2Fe3O4(s) = C(s) + 3Fe2O3), HSC predicts that significant amount of CO2(g) will be produced and only a small amount of Fe3O4 is converted to Fe2O3, (Fig. 1).
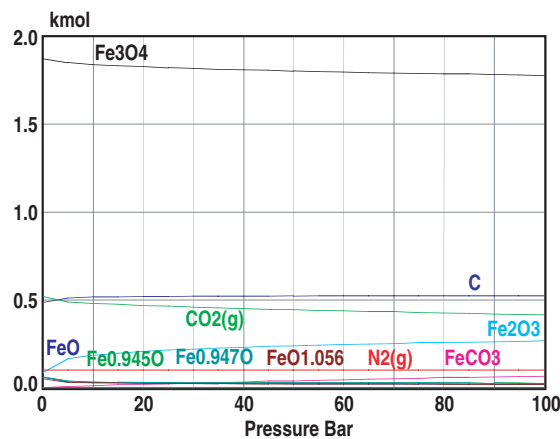
Fig. 1. Equilibrium amounts, moles, of major constituents predicted by HSC at 250°C when 1 mole of CO(g) is reacted with Fe3O4. Note that a significant quantity of CO2(g) is produced over a wide range of pressures and that only a small amount of Fe3O4 is converted to Fe2O3.

This equilibrium calculation suggests that the conversion rate for this process will be small for the amount of material that must be processed. More importantly, a parasitic reaction resulting in very stable CO2(g) can be expected. Because conversion back to CO or C is difficult (carbon dioxide is nearly as stable as water) CO or C will need to be continually supplied. **It is, therefore, concluded that this thermochemical process is impractical and has an efficiency of 0%.**

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 67 –HYBRID SULFUR

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
H2SO4	2H2SO4 = 2SO2 + 2H2O + O2(g)	1	850
SO2	SO2(g) + 2H2O(g) = H2SO4(l) + H2(g)	0.5	77

This cycle has been extensively studied. In this process SO_2 is used to lower the potential required for the electrolysis of water in Reaction SO2. The resulting H_2SO_4 is vaporized and decomposed at 850°C. The products are then separated and recycled in the process.

A detailed efficiency analysis was performed [2] including the heat and work requirements for the separation processes. Also included in these calculations are power recovery from two turbines.

The overall efficiency of this process is 50.9%.

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UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 68 – ARSENIC-AMMONIUM IODIDE

This cycle is based on the following chemical reactions from Ref. [1]:

Reaction No.	Formula	Max. Temp. (°C)
68A	$(NH_4)H_2AsO_4 = 0.5\ As_2O_3 + NH_3 + 1.5\ H_2O + 0.5\ O_2(g)$	554
68B	$0.5\ As_2O_3 + I_2 + 3NH_3 + 2.5\ H_2O = (NH_4)H_2AsO_4 + 2NH_4I$	198
68C	$2NH_4I(g) = I_2(g) + 2NH_3 + H_2(g)$	500

SUMMARY

Although the viability of this cycle would ultimately be dependent on the determination of a separation method for the reaction 68B products, the predicted thermal efficiency of the cycle is 7.9%. This is sufficiently low to preclude a more rigorous evaluation of the cycle.

A discussion of each reaction is shown below.

REACTION 68A

Calculations made with Ref. [2] show that reaction 68A is spontaneous at temperatures above 415°C, where delta G is zero. The 554°C maximum temperature specified for this reaction is adequate, but was reduced to 500°C for this assessment because equilibrium calculations indicate that the As_2O_3 and O_2 product yields reach 0.5 mole at temperatures ≥460°C. A 500°C operating temperature can be maintained with a 400.23 MJ solar heater.

REACTION 68B

The equilibrium for reaction 68B lies to the right at temperatures below 198°C. The 198°C temperature specified for Reactor 147B is at the maximum, and was reduced to 150°C for this assessment. A 150°C operating temperature can be maintained with a 124.02 MJ cooler.

The $(NH_4)H_2AsO_4$ and the NH_4I are both produced as mixed solids. Because the $(NH_4)H_2AsO_4$ is fed into Reactor 68A, and the NH_4I is fed into Reactor 68C, these products must be separated for the cycle to proceed. The boiling point of NH_4I is 405°C, but the $(NH_4)H_2AsO_4$ begins to decompose at 360°C. Both materials are soluble in H_2O, but could possibly be separated by extraction with other solvents. Unless a separation method is devised, this cycle is unworkable.

REACTION 68C

Calculations show that reaction 68C is spontaneous at temperatures above 419°C, where delta G is zero. Because HI is produced as an intermediate reaction product together with the H2, the H2 yield at the specified reaction temperature of 500°C is only 0.227 mole (Fig. 1). A 500°C operating temperature can be maintained with a 425.76 MJ solar heater.
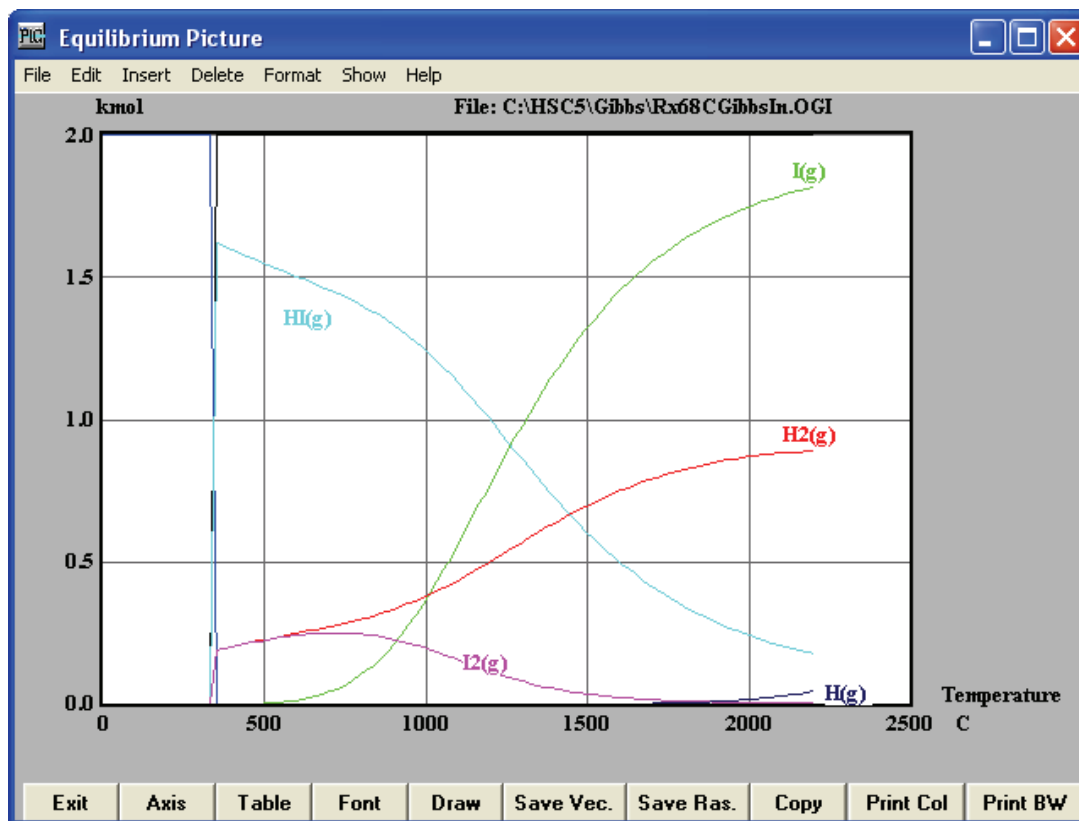
Fig. 1. Reaction 68C —2NH4I(g) = I2(g) + 2NH3(g) + H2(g)

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

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PID 70 – HYBRID SULFUR-BROMINE

The Mark 13 process is based on the following chemical reactions from the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
H2SO4	2H2SO4 = 2SO2 + 2H2O + O2(g)	0.5	850
Br2-2	Br2 + SO2 + 2H2O = 2HBr + H2SO4	1	77
HBr-2	2HBr = Br2 + H2(g)	1	77

More specific phases were used to prepare HSC 5 reaction data [1], as follows:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
H2SO4	2H2SO4(g) = 2SO2(g) + 2H2O(g) + O2(g)	0.5	850
Br2-2	Br2(l) + SO2(g) + 2H2O(l) = 2HBr(g) + H2SO4(l)	1	77
HBr-2	2HBr(g) = Br2(l) + H2(g)	1	77

SUMMARY

The overall efficiency of the process was calculated as 37.9% (using 38% conversion efficiency for production of external electricity). An ASPEN study of the H2SO4 boiling system was prepared by Ben Russ at GA which showed that about 13% of the heat required for the H2SO4 boiler system could be saved in that equipment by judicious use of heat exchangers. This improves the overall thermal efficiency to about 39.5%.

DISCUSSION

The HSC 5 data for the H2SO4 reaction are shown in Fig. 1. The temperature at which delta G is zero is about 550°C, where delta H is 191 kJ per g-mole of H2SO4 or H2, and K = 1. A simplified flow sheet for the process [2] shows 75 wt% H2SO4 coming to a concentrator, through a H2SO4 boiler at 98 wt% and entering a vertical multistage catalyst tower at the top. SO3+SO2+O2+H2O gases leave the bottom at 850°C. The data for the H2SO4 reaction at that temperature are also shown in Fig. 1.

The separation of the product gases requires an extensive equipment train, including a recombiner, a concentrator, three condensers, an absorber and three heat exchangers for separation of SO2(g) for recycle and O2(g) for release [3].

Figure 2 shows the HSC 5 data for the Br2-2 reaction, where delta G does not approach zero, delta H is about 4 and K is about 1.8E+5 at 77°C. The reactor is a vertical packed column with liquid Br2 introduced at the top and H2SO4 + H2O removed at the bottom. HBr gas is removed from the top and H2O + SO2 mixtures are introduced at two levels. The H2SO4 is concentrated and evaporated in a boiler before being introduced to the multistage tower.

The HBr-2 reaction is electrolytic. Current density cannot be increased beyond 400-450 mA/cm^2 where hydrogen and bromine bubble formation lead to cell failure in long-term operation [4].

Economic assessments of the Mark 13 process were conducted in 1981 [5] and 1985 [2], the latter assuming 912,000 GJ/yr hydrogen production (7.053 million kg/yr), using a dedicated solar receiver system operating for 2333 hrs/yr mean total sunshine hours. The Mark 13 hybrid cycle produces sufficient HBr to operate the electrolyzer for 7000 hrs/yr with externally generated electric power.

During solar operation, 89.3 MW$_{th}$ (322 GJ/hr) was estimated to be required by the H2SO4 boiler, 62.17 MW$_{th}$ (224 GJ/hr) was required by the H2SO4 decomposer and 10.8 MW$_{th}$ (39 GJ/hr) was required by the concentrator. Total solar heat input at 900°C is thus 162.3 MW$_{th}$ (584 GJ/hr). The total net electric energy consumption was estimated at 110×10^6 kWh/yr (396,000 GJ/yr).

The overall efficiency of the process was calculated as 37.9% (using 38% conversion efficiency for production of external electricity). An ASPEN study of the H2SO4 boiling system was prepared by Ben Russ at GA which showed that about 13% of the heat required for the H2SO4 boiler system could be saved in that equipment by judicious use of heat exchangers. This improves the overall thermal efficiency to about 39.5%.

The cost of the solar hydrogen was $52/GJ ($15/kg, 1984 dollars) [2]. The CPI has increased 85% since that time, so the current cost of hydrogen from the Mark 13 process can be estimated at about $96/GJ ($27.50/kg).

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[1]   S. Yalcin, "A Review of Nuclear Hydrogen Production," *Int. J. of Hydrogen Energy,* Vol. **14**, No. 8, pp. 551-561, 1989.

[2]   E. Bilgen, R.K. Joels, "An Assessment of Solar Hydrogen Production Using the Mark 13 Hybrid Process," *Int. J. of Hydrogen Energy,* Vol. **10**, No. 3, pp. 143-155, 1985.

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PID 72 – CALCIUM-IRON BROMIDE-2

This assessment of the PID 72 thermochemical process is based on the following chemical reactions in the UNLV database, with an extensive bibliography:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Br2	2Br2(g) + 2CaO = 2CaBr2 + O2(g)	0.5	600
CaBr2-3	CaBr2 + H2O = CaO + 2HBr	1	750
Fe3O4-4	Fe3O4 + 8HBr = Br2 + 3FeBr2 + 4H2O	1	300
FeBr2	3FeBr2 + 4H2O = Fe3O4 + 6HBr + H2(g)	1	600

SUMMARY

If the net 379 MJ available is sufficient to produce steam for turbine-driven compressors, the net thermal efficiency of this cycle is 40.0%. This is confirmed by Toyo Engineering Corp. at 39.4% [1]. If a high-recovery membrane can be developed and a steam turbine generator can be used to produce export power with extraction steam for the compressors, the cycle efficiency can be raised to 44.9% [5].

Based on the complication of this cycle, very high mass flows, membrane development requirements and limited prospects for further efficiency improvements, further work on this cycle does not appear to be justified.

DISCUSSION

The UNLV database includes the latest definitive flowsheet in Fig. 1 of Ref. [1]. That flowsheet is based on cyclic flow of gases at about 2 bar and about 100 moles of steam per kg-mole of H2 produced (over 890 times the mass flow) through four moving bed reactors, with membrane separators for H2 and O2. The process developers proposed that after one hour of operation in one direction, limited by the CaBr2-3 reaction, the gas flow should be reversed, sweeping the excess steam and gaseous reaction products to the next reactor. The use of dual-purpose membrane separators can be eliminated by transferring solids between two sets of two fluid bed reactors that transfer CaO-CaBr2 and Fe3O4-FeBr2 solids.

Br2 Reactor

This reaction is also used in PID 139, which was not selected for assessment. HSC-5 data shows Delta G is negative for all temperatures for this reaction, while K is higher at lower temperatures. The proposed temperature for this reaction appears to have changed during several iterations of the published conditions, but a material and energy balance allows 590°C with a heat leak of about 8 MJ per kg-mole of H2 produced. HSC-5 equilibrium data show about

0.03 moles of CaO and Br2 remain at 590°C. Pressure does not significantly affect the equilibrium.

CaBr2-3 Reactor

This reaction is also used in PIDs 3 and 139, neither of which was selected for assessment. **HSC-5 data show that delta G is positive for all temperatures below 2000°C for this reaction.** HSC-5 equilibrium data show about 0.13 moles of CaO is produced at 1500°C and 2 bar. Operation at 50 bar limits CaO production to about 0.1 moles. The heat balance for the reactor shows that an operating temperature of 705°C provides adiabatic operation with a heat leak of 7 MJ per kg-mole of H2 produced.

Fe3O4-4 Reactor

This reaction is also used in PID 62, which was assessed earlier. HSC-5 data show that delta G is negative below 619 C for this reaction, with K about 3E+8 at 300°C. HSC-5 equilibrium data show that about 0.5 moles of HBr remain at 300°C. The heat balance for the reactor shows that an operating temperature of 300°C provides adiabatic operation with a heat leak of 1.4 MJ per kg-mole of H2 produced.

FeBr2 Reactor

This reaction is also used in PIDs 62 and 139. PID 62 was assessed earlier and PID 139 was not selected for assessment. **HSC-5 data show that delta G is negative above 1399°C for this reaction,** with K slowly rising above that temperature. HSC-5 equilibrium data show that about 0.2 moles of Fe3O4 is produced at 1500°C. The heat balance for the reactor shows that an operating temperature of 452°C provides adiabatic operation with a heat leak of about 8 MJ per kg-mole of H2 produced.

Assuming that a continuous sweep of steam and gases, as reported in Refs. [2–4], can eliminate the delta G and equilibrium limitations of the CaBr2-3 and FeBr2 reactions, they can come close to the conditions proposed in Ref. [1], as shown in the following table:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Br2	2Br2(g) + 2CaO(s) = 2CaBr2(s) + O2(g)	0.5	590
CaBr2-3	CaBr2(s) + H2O(g) = CaO(s) + 2HBr(g)	1	705
Fe3O4-4	Fe3O4(s) + 8HBr(g) = Br2(g) + 3FeBr2(s) + 4H2O(g)	1	300
FeBr2	3FeBr2(s) + 4H2O(g) = Fe3O4(s) + 6HBr(g) + H2(g)	1	450

The flowsheet in Ref. [1] includes five major heat exchangers, two of which (HX1 and HX2) remove a total of 1452 MJ from the system, and three add heat. HX3 adds 1030 MJ prior to the Br2 reactor, while HX4 provides 43 MJ to produce steam from water added to the system, after it

is used to cool the product H2(g) and O2(g). The solar heater provides about 700 MJ per kg-mole of H2 prior to the CaBr2-3 reactor.

In addition, three compressors are required to provide recycle of about 100 moles of steam, and to compress byproduct O2(g) and product H2(g) for beneficial use. **If the net 379 MJ available is sufficient to produce steam for turbine-driven compressors, the net thermal efficiency of this cycle is 40.0%.** This is confirmed by Toyo Engineering Corp. at 39.4% [1]. If a high-recovery membrane can be developed and a steam turbine generator can be used to produce export power with extraction steam for the compressors, the cycle efficiency can be raised to 44.9% [5].

Based on the complication of this cycle, very high mass flows, membrane development requirements and limited prospects for further efficiency improvements, further work on this cycle does not appear to be justified.

REFERENCES

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[5] Y. Tadokoro, T. Kajiyama, N. Yamaguchi, H. Sakai, H. Kameyama, K. Yoshida, "Technical Evaluation of UT-3 Thermochemical Hydrogen Production Process for an Industrial Scale Plant," *Int. J. Hydrogen Energy,* Vol. **22**, No. 1, pp. 49-56. 1997.

PID 82 – MANGANESE-MAGNESIUM IODIDE-1

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
HI-1	2HI = I2(g) + H2(g)	1	300
I2-14	I2(s) + Mg(OH)2(s) + Mn2O3(s) = MgI2(a) + 2MnO2(s) + H2O(l)	1	27
MgI2-3	MgI2(s) + 2H2O(g) = 2HI(g) + Mg(OH)2(s)	1	227
MnO2	4MnO2(s) = 2Mn2O3(s) + O2(g)	0.5	487

SUMMARY

The proposed oxygen evolution step MnO2 is very inefficient at the proposed temperature, so the thermal efficiency is zero.

REACTION MnO2

Neither reaction I2-14 nor reaction MnO2 go to completion. Figure 1 shows the equilibrium products as a function of temperature for reaction MnO2. As can be seen, at the indicated temperature of 487ºC, only 50% of the expected ½ mole of oxygen is produced. Raising the temperature to 750ºC produces the ½ mole of oxygen and raising the temperature further increases the oxygen release.
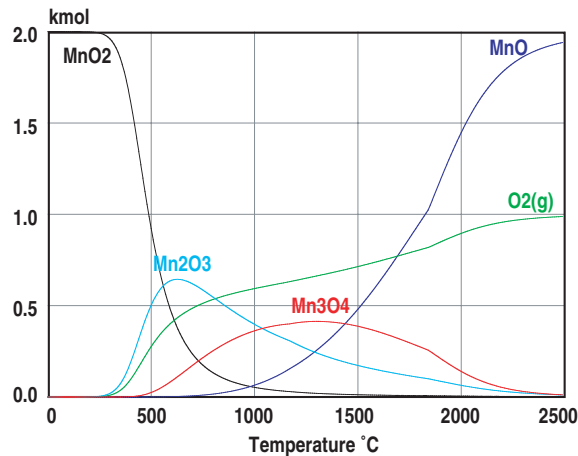
Fig. 1.

Figure 2 shows the equilibrium products from reaction I2-14 as a function of temperature. The lower the temperature, the more MnO2 is formed, but as this must be the low exothermic reaction of the cycle, the temperature must be high enough to release the heat to the environment, say 40°C. Attempting to reconcile the partial reactions, one can iterate a solution by substituting the actual manganese products from reaction MnO2 into the equilibrium calculation for reaction I2-14 and the manganese containing products from I2-14 into the equilibrium calculation for the MnO2 reaction until a stable solution is obtained. The result is very curious, as shown in Fig. 3 for the 500°C case, no oxygen is liberated until the base temperature for the calculation is reached, thus the cycle releases no oxygen at the proposed temperature and the efficiency must be zero.
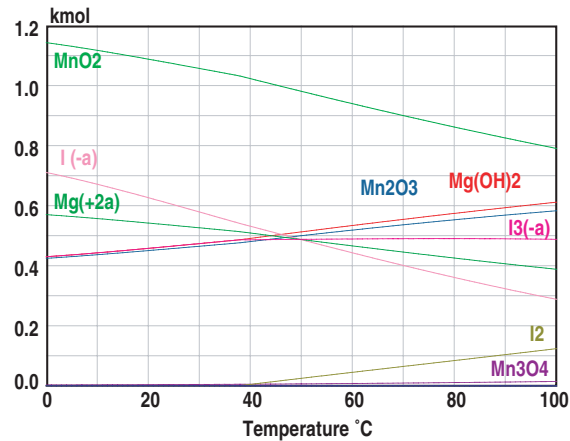
Fig. 2.
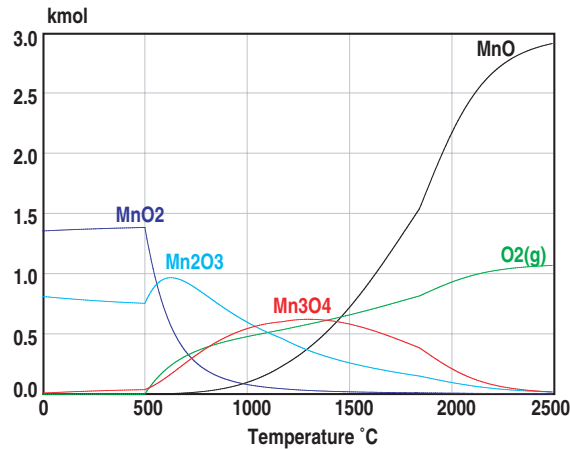
Fig. 3. Iterated solution at 500°C.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 91 – CARBON-SCANDIUM BROMIDE

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (°C)
CO-3	$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$	1.0	450
Br2-3	$6Br_2(l) + 2Sc_2O_3(s) = 4ScBr_3(a) + 3O_2(g)$	0.1666	27
CO2-5	$3CO_2(g) + 2ScBr_3(s) = 3Br_2(g) + 3CO(g) + Sc_2O_3(s)$	0.3333	1000

SUMMARY

Because delta G does not approach zero, a low-temperature electrolyzer is required for the Br2-3 reactor and Sc2O3 is insoluble, this cycle is not technically feasible.

DISCUSSION

The CO-3 reaction is the commercial water-gas shift reaction that can use a catalyst and/or absorbent to remove CO2 in situ to produce purified hydrogen. HSC-5 data indicates delta G = 0 at 817°C and K = 7.5 at the proposed 450°C operating temperature. The absorbent can be regenerated for recycle to the CO-3 reactor and the recovered CO2 can be used to fluidize the CO2-5 reactor along with steam generated during heat recovery.

HSC-5 data shows delta G for the CO2-5 reactor = 0 at 995°C. A temperature above 1000°C is required to obtain adequate kinetics for commercial operation. ScBr3 is molten above 970°C, so a fluid bed of Sc2O3 particles coated with ScBr3 is required in the reactor.

HSC-5 data shows delta G for the Br2-3 reaction does not approach 0 at any temperature, so an electrolyzer is required. However, several problems remain, including:

1. Bromine solubility in water at 30°C is 4.17 g/100cc, so a large quantity of water is required in the bath and fresh water is required to scrub the oxygen for release.

2. A chiller will be necessary to hold the temperature of the bath at 27°C where the Br2 vapor pressure is low.

3. Sc2O3 from the CO2-5 reactor is insoluble, so ion formation in the electrolyzer will be very difficult.

Because delta G does not approach zero, a low-temperature electrolyzer is required for the Br2-3 reactor and Sc2O3 is insoluble, this cycle is not technically feasible.

REFERENCES:

[1] Russell, J., Porter, J., "Production of Hydrogen from Water," General Atomics Final Report GA-A12889 HY-1205. 1974.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 93 – TUNGSTEN-ALUMINUM BROMIDE

This assessment is based on the following reactions in the UNLV database [1]:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Al2O3	2Al2O3(s) + 6Br2(l) = 4 AlBr3(ia) + 3O2(g)	0.1666	27
AlBr3-2	2AlBr3(g) + 3WO3(s) = Al2O3(s) + 3Br2(g) + 3WO2(s)	0.3333	687
WO2	WO2(s) + H2O(l) = WO3(s) + H2(g)	1	127

CONCLUSION

Equilibrium data confirm that reaction AlBr3-2 produces Al2O3, but produces no WO2 and limited Br2 at the proposed temperature, where WO3 and WBr5 are favored. Maximum production of WO2 and Br2 is predicted at about 1450°C; however, operation there limits production of Al2O3. The products from the two aqueous reactors in this cycle facilitate the addition of water for density separation and recycling of unconverted solids from the AlBr3-2 reactor; however, steam addition exacerbates the dry conversion problems. Therefore, efficiency cannot be calculated and further consideration of the PID 93 cycle appears to be unjustified.

Discussions of each reaction are shown below.

Al2O3 Reactor

HSC-5 data for the exothermic Al2O3 reaction show delta G is negative below 54 C. This reactor can be operated at 27 C where K is about 117, without an electrochemical step.

AlBr3-2 Reactor

HSC-5 data for the slightly exothermic AlBr3-2 reaction is negative at all temperatures, with slow kinetics. HSC-5 equilibrium data shows complete AlBr3 conversion to Al2O3 at 687°C and 2 bar; however, Br2 production and WO3 conversion to WO2 is limited by the formation of WBr5(g). Maximum conversion of WO3 is reached at about 1450°C, where about 0.65 moles of WO2 and 0.27 moles of WO3 remain. However, at 1450 C AlBr3 is about 0.22 moles and Al2O3 is about 0.22 moles. Pressure shows no effect on the results. These results check against Eguilib-Web ChemSage equilibrium data at 687°C and 1450°C at 2 bar, with the following results:

Compound	Moles @ 687 C	Moles @ 1450 C
Br2 + Br	0.171	0.861
AlBr3	0.005	0.218
Al2O3	0.3333	0.224
WBr5	0.328	0.009
WO3	0.669	0.274
WO2 + W	0	0.649

Solids separation for Al2O3, WO2 and WO3 to recycle must depend on the density differences among them at low temperatures, such as froth flotation. Therefore, the effect of water and steam for transport and separation of solids on the equilibria was investigated using Eguilib-Web ChemSage equilibrium data at 687°C and 1450°C at 2 bar. The equilibria for the AlBr3-2 reaction in the presence of 10 moles of H2O(g) show the following product:

Compound	Moles @ 687°C	Moles @ 1450°C
Br2	9.56E-4	4.9E-3
H2O	9.000	8.279
H2	1.08E-3	7.5E-2
HBr	1.998	1.85
AlBr3	negligible	negligible
Al2O3	0.3333	0.3333
WBr5	negligible	negligible
WO3	0.999	1
WO2	negligible	0

These data show that steam addition increases the yield of Al2O3 at 1450°C, but produces HBr instead of Br2 and minimizes conversion of WO3. In addition, the use of water to transport and separate solids requires solar drying to minimize water addition to the AlBr3-2 reactor.

WO2 Reactor

HSC-5 data for the WO2 reaction show that delta G is negative above 113°C in an aqueous environment, where the hydrolysis of WO2 is slow. H2(g) must be continuously withdrawn to avoid equilibrium limitations on conversion.

REFERENCES

[1] John L. Russell, Jr., John T. Porter, II. "Production of Hydrogen from Water," General Atomics Final Report GA-A12889, 1974

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 103 –CERIUM CHLORIDE

This cycle is based on the following chemical reactions from Ref. [1]:

Reaction No.	Formula	Max. Temp. ($^{\circ}$C)
103A	$Cl_2(g) + H_2O(g) = 2HCl(g) + 0.5\ O_2(g)$	800
103BC	$2CeCl_3 + 4H_2O = 2CeO_2 + 6HCl(g) + H_2(g)$	450
103D	$2CeO_2(s) + 8HCl(g) = 2CeCl_3(s) + Cl_2(g) + 4H_2O$	25

Properties of significant compounds in this cycle are:

Compound	MP (°C)	BP (°C)
CeCl3	817	1727
CeO2	2400	ca 2600

SUMMARY

The calculated thermal efficiency of PID 103 is predicted to be 21.2%. This is sufficiently low to preclude a more rigorous evaluation of the cycle.

Discussions of each reaction along with a simplified flowsheet (Fig. 1) are shown below.

REACTION 103A

Calculations made with the Ref. [2] program show that reaction 103A is spontaneous at temperatures above 595°C, where delta G is zero. The 800°C maximum temperature specified for this reaction is adequate, but was increased to 1450°C for this assessment because equilibrium calculations indicate that the O2 product yield reaches a maximum of 0.415 mole at 1450°C. This yield is low because the reaction is incomplete. The 1450°C operating temperature can be maintained with a 136.87 MJ solar heater.

The Reactor 103A offgas mixture is cooled to 25°C in Offgas Cooler 103A. Ninety nine percent of the 114.33 MJ heat from this cooler is recuperated in CeCl3 Dryer 103D. The 1% excess heat from Offgas Cooler 103A is rejected.

REACTION 103B

The equilibrium for reaction 103B lies to the right at temperatures at or above 424°C. The 425°C temperature specified for Reactor 103B is only slightly above the minimum, and should be increased to achieve better kinetics.
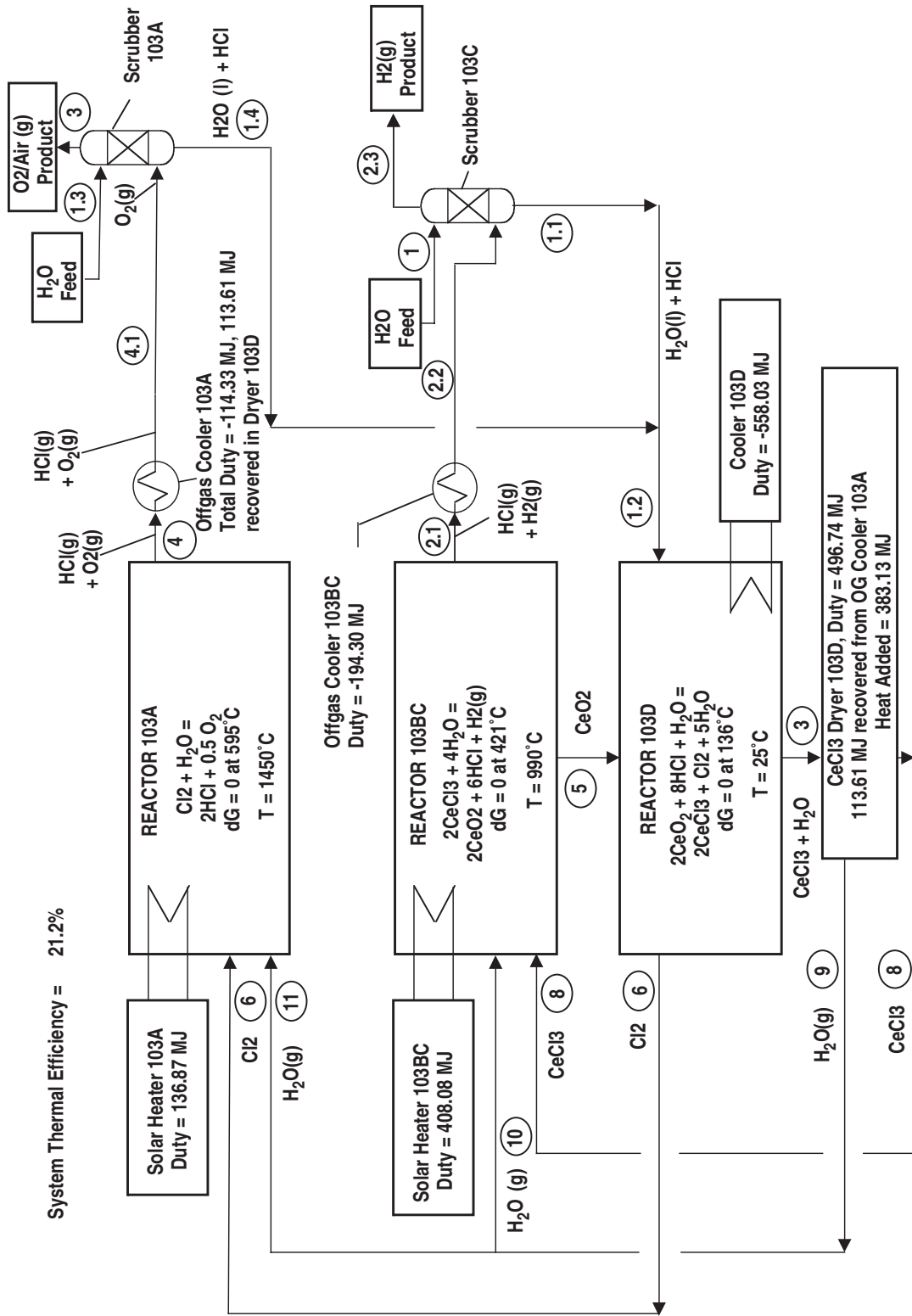
Fig. 1. Solar hydrogen generation project, PID 103 flowsheet, rev. 2.

Equilibrium calculations for this reaction indicate that the reaction is incomplete, and produces only 0.370 moles CeClO.

REACTION 103C

Using the 2 moles of CeClO reactant specified in the Ref. [1] databases, reaction 103C is spontaneous at temperatures above 419°C, where delta G is zero. The 450°C maximum temperature specified for this reaction is adequate, but was increased to 850°C for this assessment because equilibrium calculations indicate that the H2 product yield reaches a maximum of 0.819 moles at this temperature. When the calculated equilibrium product mixture of reaction 103B is input into reaction 103C, however, H2 production decreases to 0.419 moles.

REACTION 103BC

Because the CeClO product from reaction 103B is a reactant for reaction 103C, these reactions were combined into reaction 103BC and recalculated. It was determined that delta G is negative above 421°C and H2 production increases to 0.687 mole at 990°C for the combined reaction. Hydrogen production is less than the predicted 1 mole yield because the reaction is incomplete (Fig. 2 – Reaction 103BC Equilibrium Picture). The 990°C operating temperature can be maintained with a 408.08 MJ solar heater.
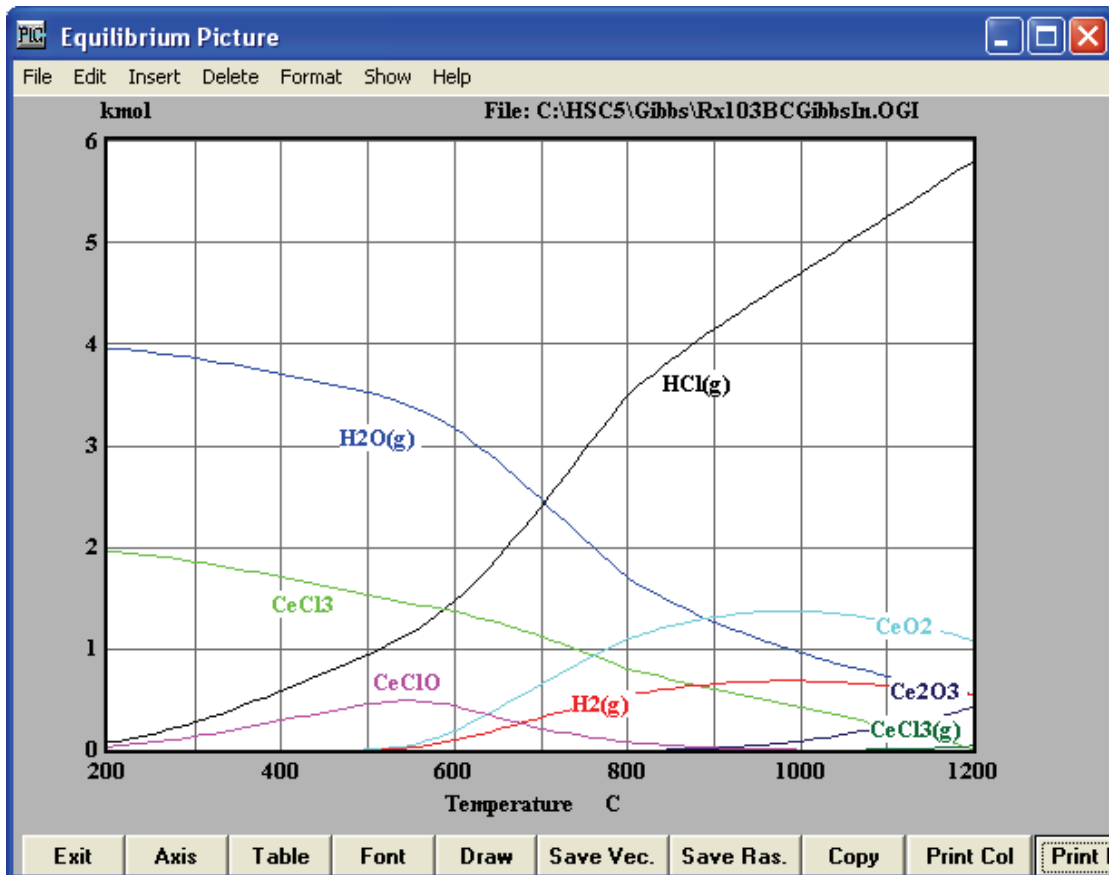
Fig. 2. Reaction 103bc equilibrium picture —Combined Reactions 103B and 103C into Reaction 103BC 2CeCl3 + 4H2O = 2CeO2 + 6HCl(g) + H2(g).

The calculated equilibrium output from reaction 103BC was used to complete the assessment.

REACTION 103D

The equilibrium product mixture of reaction 103BC together with the 1.66 moles HCl from reaction 103A and the 1 mole feedwater are fed into reactor 103D. This reaction is spontaneous at temperatures below 136°C where delta G = 0. The 25°C operating temperature specified in Ref. [1] is adequate. The exotherm from reaction 103D together with the heat content in the reactants requires a 558.03 MJ cooler to maintain 25°C in the reactor.

The H_2O and $CeCl_3$ from reactor 103D are separated in Dryer 103D where 113.61 MJ heat is recouperated from Offgas Cooler 103A and 383.13 MJ heat is added to increase the temperature of the products to 700°C.

REFERENCES

[1]   John L. Russell, Jr., John T. Porter, II. "Production of Hydrogen from Water," General Atomics Final Report GA-A12889, 1974.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 104 –MAGNESIUM-CERIUM CHLORIDE

This cycle is based on the following chemical reactions from Ref. [1]:

Reaction No.	Formula	Max. Temp. (°C)
104A	Cl2(g) + Mg(OH)2(s) = MgCl2(aq) + H2O(l) + 0.5 O2(g)	50
104B	4MgCl2(a) + 8H2O = 8HCl + 4MgO + 4H2O	650
104CD	2CeCl3(a) + 3Mg(OH)2(ia) = 2CeO2 + 3MgCl2(a) + 2H2O + H2(g)	50
104E	2CeO2(s) + 8HCl(g) = 2CeCl3(s) + Cl2(g) + 4H2O	50

Properties of significant compounds in this cycle are:

Compound	MP (°C)	BP (°C)	H2O Solubility [grams/liter at (°C)]
CeCl3	817	1727	1000 (20)
CeO2	2400	ca 2600	Insoluble
Ce2O3	2230	3227	Insoluble
Mg(OH)2	-H2O, (350)		0.009 (18), 0.04 (100)
MgO	2800	3600	0.0062 (20), 0.086 (80)
MgCl2	714	1412	542 (30), 727 (100)

SUMMARY

The calculated thermal efficiency of PID 104 is predicted to be 17.9%. This is sufficiently low to preclude a more rigorous evaluation of the cycle.

Because of the numerous interactions among the reactions in this cycle, a more precise assessment could be performed by modeling it in the Aspen (or equal) program.

Discussions of each reaction along with a simplified flowsheet for this cycle (Fig. 1) are shown below.

REACTION 104A

Calculations made with Ref. [2] show that reaction 104A is spontaneous at temperatures below 476°C, where delta G is zero. The 25°C maximum temperature specified for this reaction

is adequate, but was increased to 50°C for this assessment to provide a delta T for Cooler 104A when it is operating at a duty of -208.12 MJ.

System Thermal Efficiency = 17.9%

Scrubber 104A

$O_2(g)$ Product (3.1)

$H_2O(l)$ (1.1)

H_2O Feed (1)

$O_2(g)$ (3)

$8HCl(g)$ (xx)

$8HCl(g) + 4H_2O$

Offgas Cooler 104B & H_2O/HCl Separator Duty = -401.37 MJ Heat recovered in Dryer 104E = 134.75 MJ

$H_2(g)$ Product (2.1)

H2 Cooler 104CD Duty = -0.68 MJ (2) $H_2(g)$

Cooler 104E Duty = -408.77 MJ

REACTOR 104A
$Cl_2(g) + Mg(OH)_2 = MgCl_2(a) + H_2O(l) + 0.5 O_2(g)$
$dG \leq 0$ at $\leq 476°C$
T = 50°C

(4) $0.871 MgCl_2(a) + 1.000 H_2O(l) + 0.095 MgCl(+a) + 0.034 Mg(+2a)$

REACTOR 104B
$4MgCl_2(a) + 8H_2O = 8HCl(g) + 4MgO + 4H_2O$
$dG \leq 0$ at $\leq 275°C$
T = 650°C

$4H_2O$ (xx)

$4MgO$ (xx)

$3Mg(OH)_2$

REACTOR 104CD
$2CeCl_3(a) + 3Mg(OH)_2(ia) = 2CeO_2 + 3MgCl_2(a) + 2H_2O + H_2(g))$
$dG \leq 0$ at $\leq 1358°C$
T = 50°C

$3MgCl_2 + 2CeO_2 + 2H_2O$ (xx)

Filter

$2CeO_2$ (xx)

REACTOR 104E
$2CeO_2 + 8HCl = 2CeCl_3 + Cl_2 + 4H_2O$
$dG \leq 0$ at $\leq 136°C$
T = 50°C

$8HCl(g)$ (xx)

Cooler 104A Duty = -208.12 MJ

$Mg(OH)_2$ (xx) Cl_2 (xx)

Solar Heater 104B Duty = 1509.49 MJ

$4H_2O(g)$ (xx)

$3MgCl_2 + 2H_2O$ (xx)

Cooler 104CD Duty = -3.84 MJ

$2CeCl_3$ (xx)

$3MgCl_2 + 2H_2O$

Cl_2 (6)

$2CeCl_3 + 4H_2O$

CeCl3 Dryer 104E Duty = 134.75 MJ All Heat is recovered from OG Cooler 103B

Fig. 1. PID 104 flowsheet, Rev.1.

REACTION 104B

The equilibrium for reaction 104B lies to the right at temperatures above 275°C where delta G = 0. The 450°C temperature specified for Reactor 104B was increased to 650°C for this assessment because equilibrium calculations indicate that the MgO and HCl product yields reach maxima of 4.00 mole and 7.91 mole at 620°C. A 1509.49 MJ solar heater is required to maintain

the 650°C operating temperature. Because this high heat input requirement reduces the thermal efficiency of this cycle to 17.9%, further assessment of the PID 104 cycle appears unjustified.

The Reactor 104B offgas mixture is cooled to 50°C in Offgas Cooler 104B. Thirty three percent of the 401.37 MJ heat from this cooler is recuperated in CeCl3 Dryer 104E. The 66% excess heat from Offgas Cooler 104B is rejected.

REACTION 104C

Reaction 104C is specified with aqueous reactants that produce Ce2O3 + 3MgCl2 + 3 moles H2O product. When one of the 3 moles H2O product reacts with the Ce2O3, the reaction becomes Reaction CD.

REACTION 104D

Reaction 104D uses the Ce2O3 product together with 1 mole of the 3 moles H2O product from reaction 104C to produce H2. This reaction was combined with reaction 104C to become Reaction 104CD.

REACTION 104CD

In this assessment, reactions 104C and 104D are combined to form Reaction 104CD.

Delta G calculations show that reaction 104CD is spontaneous at temperatures below 1358°C, where delta G is zero. The 25°C maximum temperature specified for this reaction is adequate, but was increased to 50°C for this assessment to provide a delta T for Cooler 104CD when it is operating at a duty of -3.84 MJ.

Equilibrium calculations indicate that the product yield is 1.890 moles CeO2, 2.830 moles MgCl2, 1.888 moles H2O, and 0.943 moles H2 at the 50°C operating temperature (Fig. 2). Of the 2CeCl3 and 3Mg(OH)2 input reactants, 0.114 CeCl3 and 0.171Mg(OH)2 remain unreacted. H2 Cooler 104CD rejects 0.68 MJ heat when it cools the H2 product from 50°C to 25°C.

REACTION 104E

The equilibrium product mixture from reaction 104CD together with the HCl from reaction 104B are fed into reactor 104E. This reaction is spontaneous at temperatures below 136°C where delta G = 0. The 25°C operating temperature specified in Ref. [1] is adequate, but was increased to 50°C for this assessment to provide a delta T for Cooler 104E. The exotherm from reaction 104E together with the heat content in the reactants requires -408.77 MJ cooling to maintain 50°C in the reactor.

The H2O and CeCl3 from reactor 104E are separated in Dryer 104E where 134.75 MJ heat is recouperated from Offgas Cooler 104B to increase the temperature of the products to 200°C.
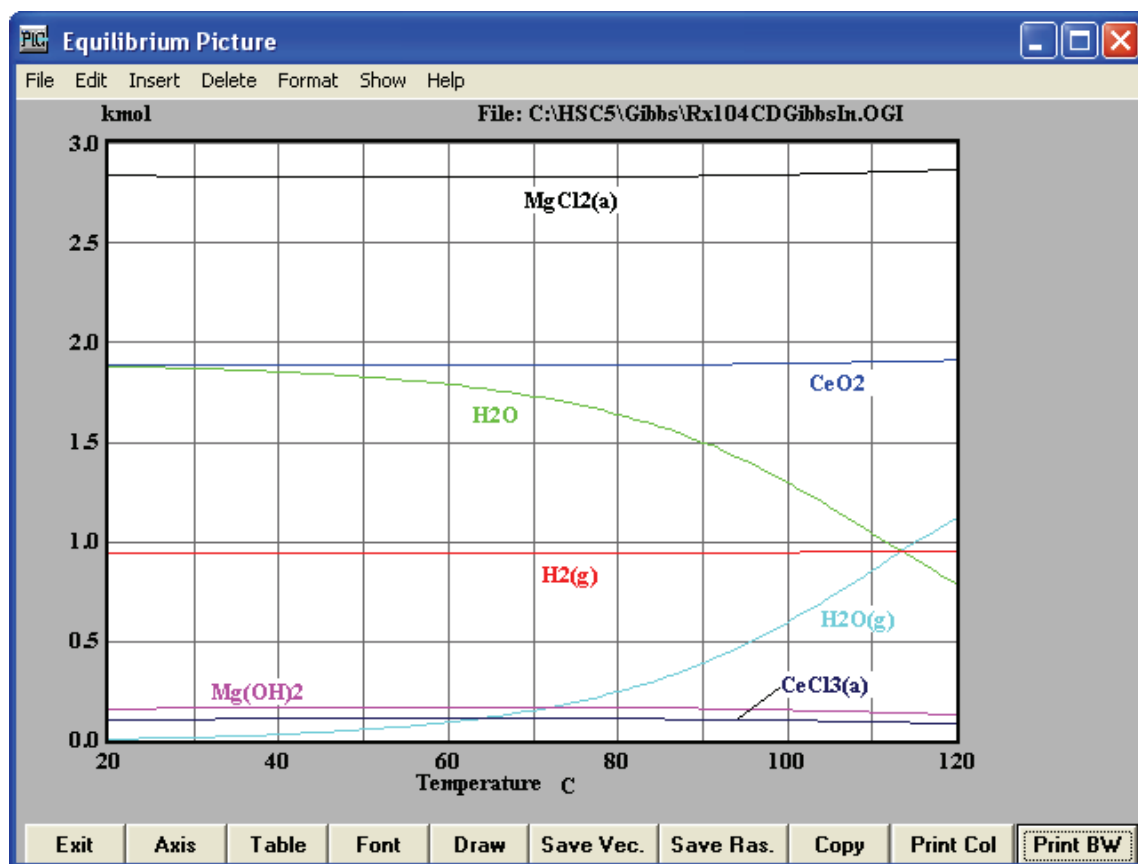
Fig. 2. Reaction 104cd equilibrium picture. Reaction 104CD is spontaneous below 1358°C. delta G = 0 at 1358°C (1631 K). 2CeCl3(a) + 3Mg(OH)2(ia) = 2CeO2 + 3MgCl2(a) + 2H2O + H2(g)

REFERENCES

[1]   John L. Russell, Jr., John T. Porter, II. "Production of Hydrogen from Water," General Atomics Final Report GA-A12889, 1974.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 105 – MANGANESE-ETHANE-ETHYLENE

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
C2H4	C2H4(g) + H2O + Mn2O3 = C2H6 + 2MnO2	1	(none viable)
C2H6	C2H6(g) = C2H4(g) + H2(g)	1	800
MnO2	4MnO2(s) = 2Mn2O3(s) + O2(g)	0.5	487

SUMMARY

Reaction C2H4 produces Mn2O3, Mn3O4 and MnO2, and their separation appears to be very difficult.

This cycle, therefore, is not technically feasible as proposed. No efficiency can be calculated based on the C2H4 reaction, for which there is no temperature at which delta G = 0, and an electrochemical reaction is not feasible.

DISCUSSION

There are no references listed for this cycle and none were found in a search of the International Journal of Hydrogen Energy or Internet search.

The C2H4 reaction is unique to this cycle. HSC-5 data for the C2H4 reaction show delta G > 0 for all temperatures below 3000°C. HSC equilibrium data show unreacted steam, methane, carbon, hydrogen and Mn3O4 in equilibrium concentrations above 400°C at 1 to 50 bar. ASPEN-PLUS data show an equilibrium composition of 0.51Mn2O3 + 0.244Mn3O4 and 0.244MnO2 + unreacted steam and ethylene, plus traces of H2, methane, ethane and propane at 50 bar and 900°C. Fractional distillation and recycling of these products to produce ethane and selective oxidation of the Mn2O3 appear to be technically infeasible.

The C2H6 reaction is also proposed in PID 159. HSC-5 data for the C2H6 reaction show delta G < 0 above 798°C, with adequate kinetics above about 900°C. The duty for the reactor is a minimum of 145 MJ for discharge at the proposed temperature per kg mole of H2 with dry feed, requiring an input/output heat exchanger prior to a selective condenser for separation of H2 from C2H4 and recycle of unreacted C2H6.

The MnO2 reaction is also proposed in PIDs 14, 15, 82, 83, and 168. HSC-5 data for the MnO2 reaction show delta G < 0 above 510°C, with adequate kinetics above about 600°C. The duty for this reactor is a minimum of 166 MJ, requiring an input/output heat exchanger for the solids and release of O2(g). However, as shown for reaction C2H4, Mn2O3, Mn3O4 and MnO2 can all be expected at these conditions, and their separation appears to be very difficult.

Therefore, this cycle is not technically feasible as proposed. No efficiency can be calculated based on the C2H4 reaction, for which there is no temperature at which delta G = 0, and an electrochemical reaction is not feasible.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 106 – High Temperature Electrolysis

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
H2O	2H2O = 2H2(g) + O2(g)	0.5	2340

The Delta G for H2O = 0 at 4250°C. For this reason, electrolysis is used to drive the reaction. The current efficiency for H2O is 98% at 1000°C, however limitations in the proton conductive electrode limit the electrochemical efficiency to around 70%.

Utilizing the recovered heat from the electrolysis cell, the solar energy required for steam generation is only 39.81 MJ and 4.4MJ. The electrical energy required for 70% efficiency electrolysis cell is 253.5 MJ, with -76 MJ of heat added by the electrolysis. An additional 8 MJ is required to increase the pressure to 2 atm.

The efficiency for this process at 1000°C is 58% as described in the attached flowsheet.

REFERENCES

[1] H. Arashi, H. Naito And H. Miura, "Hydrogen Production From High-Temperature Steam Electrolysis Using Solar Energy" Int. J. Hydrogen Energy, Vol. **16**. No. 9, Pp. 603 608, 1991.

[2] H. Iwahara, H. Uchida And I. Yamasaki, "High-Temperature Steam Electrolysis Using Srceo3-Based Proton Conductive Solid Electrolyte" Int. J. Hydrogen Energy, Vol. **12**, No. 2, Pp. 73-77, 1987.

Stream	1	2	2a	3	4	5	6
Temp °C	25	900	1000	1000	200	1000	200
Pressure (Bar)	11222	1	1	1	1	2	2
H2O kmol	1	1	1			0.3	0.3
H2 kmol				1	1		
O2 kmol						0.5	0.5
Eff	58.02%						

Electrical 70% efficiency

253.5 MJ
-76 MJ

Electolysis

8MJ

4.4MJ

39.81 MJ

Heat Exchanger 25 °C to 1000 °C

H2O   H2   O2
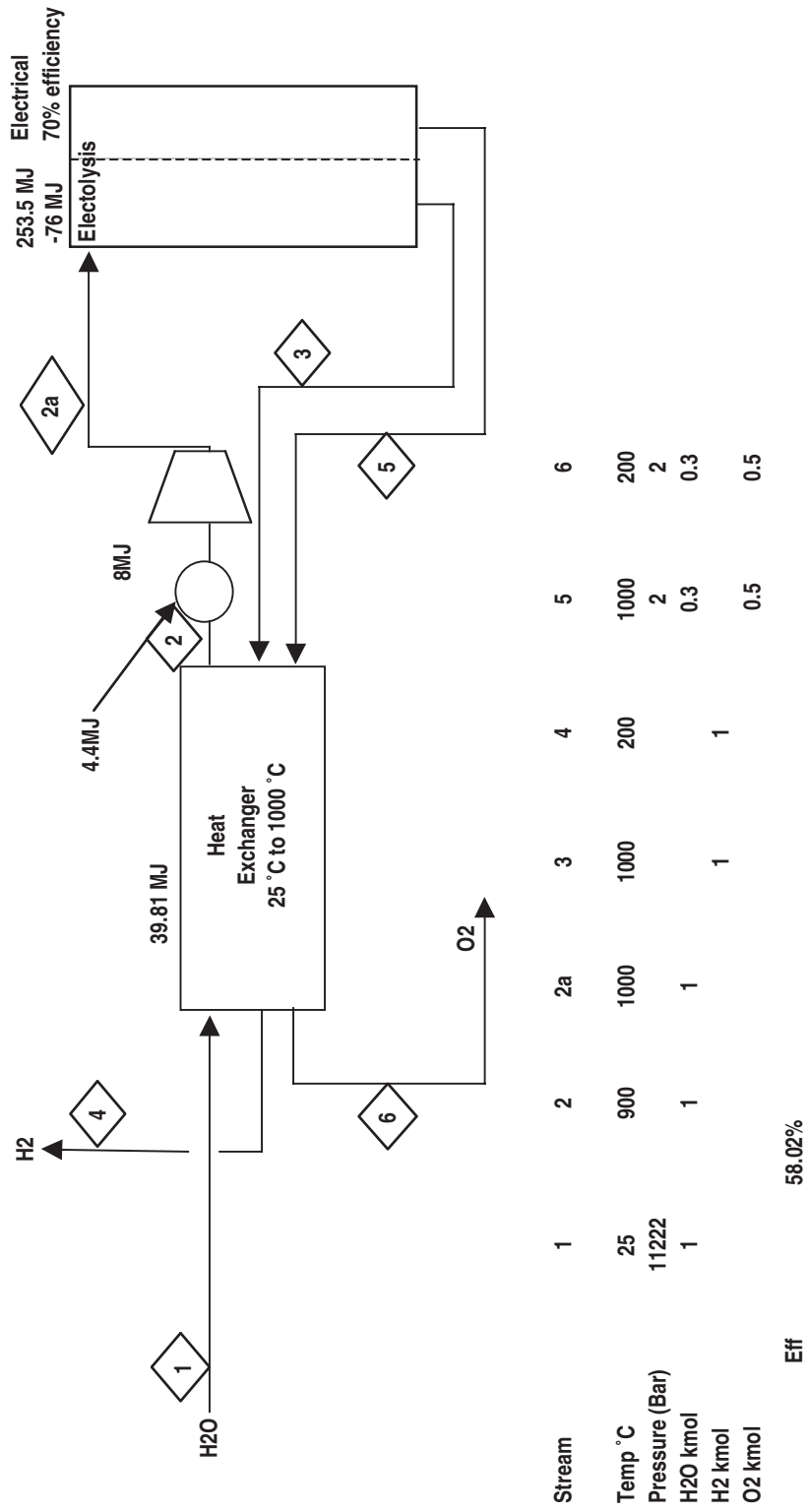
UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 110 – SODIUM MANGANESE-3

This process is based on the following reactions:

Reaction Code	Formula	Multiplier	Temp (C)
a-NaMnO2	2a-NaMnO2 + H2O = Mn2O3 + 2NaOH(a)	1	100
Mn2O3-3	2Mn2O3 = 4MnO + O2(g)	0.5	1560
MnO	2MnO + 2NaOH = 2a-NaMnO2 + H2(g)	1	630

The efficiency of this cycle was estimated as 50% in Ref. [1], using data from Ref. [2]. The paper infers a lower heating value based on H2O(g).

[1] Private communication from Prof. Alan Weimer & Chris Perkins, University of Colorado, to Lloyd Brown of General Atomics, 11-16-2004.

[2] M.Sturzenegger & P. Nuesch, "Efficiency Analysis for a Manganese-Oxide-Based Thermochemical Cycle," Energy, 24, 959-970, 1999.

PID 111 – Sodium-Manganese Ferrite-1

This process is based on the following chemical reactions:

Reaction Code	Formula	Multiplier	Proposed Temp. (°C)
MnFe2O4	2MnFe2O4(s) + 3Na2CO3(s) + H2O(g) = 2Na3MnFe2O6(s) + 3CO2(g) +H2(g)	1	1000
Na3MnFe2O6	4Na3MnFe2O6 + 6CO2 = 4MnFe2O4 + 6Na2CO3 + O2(g)	0.5	600

ANALYSIS

The exact composition and phase of the metal oxide mixture formed in the hydrogen generation step is unknown. In order to perform a thermodynamic analysis, it was necessary to assume that the metal oxide mixture could consist of any number of compounds found in the HSC-5 database containing Mn, Na, Fe, and O. The results of the analysis are shown in Fig. 1. The analysis, which was carried out over temperatures ranging from 100°C to 1000°C, showed MnFe2O4 dissociation and very little hydrogen production (1e-4 kmol). Experimental results indicate that a larger hydrogen yield is possible [1].
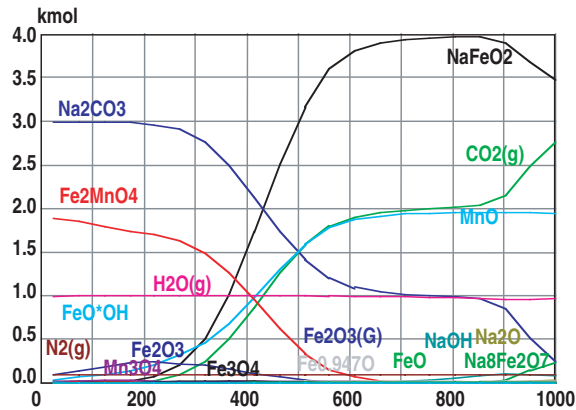
Fig. 1. Hydrogen production reaction, 1E-5 atm hydrogen pressure

An analysis of the reaction between the products of the hydrogen generation step at temperatures up to 1000°C, and assuming all hydrogen was removed, showed almost no oxygen formation. This is consistent with experimental results and is the reason why this process is not viable with regard to hydrogen production. Decreasing the pressure to 1E-6 atm does increase oxygen formation, but not substantially. **This cycle is, therefore, determined to not be viable and has an efficiency of 0%.**

ADDITIONAL COMMENTS

Tamaura *et al.*, indicate that the PID 111 process can be modified to facilitate Na3MnFe2O6 decomposition by reacting with Fe2O3 and increasing the temperature to 1000°C (PID 153). This modification requires the addition of another thermochemical step and will only proceed when the oxygen partial pressure is maintained at or below 1E-6 atm [2].

REFERENCES

[1]   Y. Tamaura, Y. Ueda, J. Matsunami, N. Hasegawa, M. Nezuka, T. Sano, "Solar Hydrogen Production While Using Ferrites," *Solar Energy,* Vol. **65**, No. 1, pp. 55-57. 1999.

[2]   H. Kaneko, Y. Hosokawa, N. Gokon, N. Kojima, N. Hasegawa, M. Kitamura, Y. Tamaura, "Enhancement of O2-releasing step with Fe2O3 in the water splitting by MnFe2O4-Na2CO3 system," *J. Phys. Chem. Solids,* Vol. **62**, No. 7, pp. 1341-1347.

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PID 112 – SWEDEN FE-CL ASSESSMENT, REV. 2

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
FeCl2-5	3FeCl2 + 4H2O(g) = Fe3O4 +6HCl(g) + H2(g)	1.0	650
Fe3O4-1	2Fe3O4 + 12HCl(g) = 6FeCl2(g) + 6H2O(g) + O2(g)	1.0	1530

SUMMARY

Commercial operation of the Fe3O4-1 reactor requires high-temperature gas separation to produce three separate streams: FeCl2(g) to the FeCl2-5 reactor, O2(g) out, and recycling the remaining products back to the Fe3O4-1 reactor [2]. **High-temperature gas separation for the Fe3O4-1 reactor is not technically feasible at this time.**

DISCUSSION

FeCl2-5 Reactor

The FeCl2-5 reaction is common to all of the proposed Fe-Cl cycles [1]. For this reaction, delta G < 0 only between 1023°C where FeCl2 is a gas and 1168°C, above which delta G is positive. The solar duty for this condition would be 601 MJ.

An electrochemical reactor eliminates the HCl(g) separation problem and the solar energy requirement by operating at 100°C, where the heat balance is neutral when the reactants are cooled and FeCl2(a) and water are fed at 60°C. Electrochemical energy required is a minimum of 250 MJ of source energy at 50% source efficiency and 329 MJ at 38% source efficiency.

Fe3O4-1 Reactor

HSC-5 data shows that delta G for this reaction is negative above 2630°C. Commercially significant quantities of O2(g) do not occur below about 1530 C via this reaction [2]. Below about 1130 C, production of O2(g) is completely eliminated by the formation of Fe2O3 via the following reaction:

$$2Fe3O4 + 4HCl(g) = 2FeCl2(g) + 2Fe2O3 + 2H2O(g). \tag{1}$$

This reaction occurs when the products of the proposed Fe3O4-1 reaction are cooled below 1230°C, and no Fe3O4 remains below about 650 C. Commercial operation of the Step 2 (Fe3O4-1) reactor requires high-temperature gas separation to produce three separate streams: FeCl2(g) to the Step 1 (FeCl2-5) reactor, O2(g) out, and recycling the remaining products back to the Step

2 (Fe3O4-1) reactor [2]. High-temperature gas separation for the Fe3O4-1 reactor is not technically feasible at this time.

REFERENCES

[1]   W. Hoogstoel, W. Goosens, A. Francesconi, L. Baetle, L., "Chemical Engineering Assessment of the Thermochemical Cycle Mark 9," *Int. J. Hydrogen Energy,* Vol. **4**, pp. 211-222. 1979.

[2]   M. Lundberg, "Model Calculations on Some Feasible Two-Step Water Splitting Processes," *Int. J. Hydrogen Energy,* Vol. **18**, No. 5, pp. 369-376. 1993.

PID 114 – HYBRID NITROGEN-IODINE

This assessment is based on the following reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
HNO3-1	2HNO3 + 2KI = 2KNO3 + I2 + H2(g)	1	25 (electrochemical)
I2-4	I2 + 2KNO3 = 2KI + 2NO(g) + 2O2(g)	1	700
NO	2NO(g) + O2(g) = 2NO2(g)	1.5	100
NO2-1	3NO2(g) + H2O = 2HNO3(a) + NO(g)	1	100

In order to determine the correct phases for these reactions, the melting and boiling points of the reactants and products must be considered, as follows:

Compound	MP	BP
HNO3	-41 C	84 C
KNO3	334 C	400 C
KI	681 C	1323 C
I2	114 C	185 C

Using these data in the reactions at the proposed temperatures and appropriate pressures results in the following table:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
HNO3-1	2HNO3(a) + 2KI(a) = 2KNO3(ia) + I2 + H2(g)	1	25 (electrochemical)
I2-4	I2(g) + 2KNO3(g) = 2KI(l) + 2NO(g) + 2O2(g)	1	700
NO	2NO(g) + O2(g) = 2NO2(g)	1.5	100
NO2-1	3NO2(g) + H2O(l) = 2HNO3(a) + NO(g)	1	100

SUMMARY

If the complex separations required by this cycle could be solved, the solar heating and the electrochemical energy requirement reduces the calculated PID 114 cycle efficiency to a

maximum of 33.3%. Therefore, further consideration of the PID 114 hybrid cycle appears unjustified.

HNO3-1 REACTOR

HSC-5 data for the HNO3-1 reaction show delta G is +88 MJ/kg-mole of H2 produced, resulting in an electrical energy requirement of 169 MJ at the hydrolyser and 339 MJ at a source with 50% generating efficiency. This was confirmed experimentally [1].

I2-4 REACTOR

HSC-5 data for the I2-4 reaction show delta G is negative above 366°C. HSC-5 equilibrium data does not exist for this reaction; however, Eguilib-Web equilibrium data at 700°C and 2 bar show the following equilibrium product composition:

Compound	moles
O2	0.75
N2	0.25
KI	0.194E-03
(KI)2	0.884E-04
NO	0.278E-04
NO2	0.474E-05

These data also show both elevated pressure and lower temperature produce less KI and NO. Experimental data showed that argon flow through a bench-scale apparatus decreased the yield of KI, which was acceptable above 1000 K [1]; however, no means was suggested of removing the nitrogen and N-O compounds from the product oxygen for introduction to the NO reactor, or of nitrogen makeup to the cycle.

Operating the I2-4 reactor at elevated temperature requires preheating, evaporation of associated water and vaporization of the products from the HNO3-1 reactor. A counter-flow preheat exchanger can increase the temperature of the reactants flowing to the I2-4 reactor to 400°C, resulting in a solar duty for the I2-4 reactor of 520 MJ/kg-mole of H2 produced.

REFERENCES

[1]   K. Tanno, X. Liao, A. Yashiro, A. Ikenoya, N. Kumagai, "Studies of the KNO3-I2 Hybrid Cycle for Hydrogen Production," *Int. J. Hydrogen Energy,* Vol. **13**, No. 5, pp. 289-298. 1988.

PID 124 – COPPER SULFATE-1

This process is based on the following proposed chemical reactions from the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (°C)
Cu-2	2 Cu(s) + H2O(g) = Cu2O(s) + H2	1	500
Cu2O-4	2Cu2O(s) + 4SO2 + 3O2 = 4 CuSO4(l)	0.33	300
Cu2O-5	2Cu2O(s) + 8 CuSO4(l) = 12 Cu(s) + 8 SO2 + 9 O2	0.17	500

SUMMARY

HSC-5 data for the Cu-2 reaction show that delta G does not approach 0 at temperatures below 2000°C. HSC-5 equilibrium data confirm this by showing show no significant H2(g) production below 2000°C. Since both Cu and Cu2O are insoluble in water, this reaction is not suitable as an electrochemical step. **The proposed cycle, therefore, is not technically feasible.**

DISCUSSION

There are no references for the proposed cycle listed in the UNLV database and the reactions are unique to the proposed cycle. Design of the reactors, separators and heat exchangers for this cycle depend on the solubility, melting and boiling points of the materials from the CRC and HSC-5, as follows:

Compound	M.P., C	B.P., C	Solubility in H2O
Cu	1085	2563	Insoluble
Cu2O	1235	?	Insoluble
CuSO4	805	?	Soluble

Cu-2 Reactor

HSC-5 data shows that delta G does not approach 0 at a temperature below 2000°C. HSC-5 equilibrium data confirms this by showing show no significant H2(g) below 2000°C. Since both Cu and Cu2O are insoluble in water, this reaction is not suitable as an electrochemical step. Therefore the proposed cycle is not technically feasible.

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PID#: 126 – CESIUM AMALGAM-2

This process is based on the following chemical reactions from Ref. [1]:

Reaction No.	Reaction Code	Formula	Multiplier	Max. Temp. (˚C)
126C	CsHg	2CsHg + 2H2O = 2CsOH +2Hg + H2	1	0
126B	CsO	CsO2 + 3Hg = CsHg + 2HgO	2	300
126D	CsOH-1	4CsOH + 3O2(g) = 4CsO2 + 2H2O	0.5	410
126A	HgO	2HgO(l) = 2Hg(g) + O2(g)	2	600

Properties of significant compounds in this cycle are:

Compound	MW	MP (°C)	BP (°C)	H2O Solubility [grams/liter at (°C)]
Hg	200.59	-38.87	356.58	Insoluble
HgO	216.59	d. 500		0.053 (25), 0.395 (100)
Cs	132.905	28.4	678.4	Decomposes
CsO2	164.90	432		
CsOH	149.91	272.3		3955 (18)
Cs2O	281.81	d. 400		

REACTION 126A:

Calculations made with Ref. [2] show that reaction 126A is spontaneous at temperatures above 475°C, where delta G is zero. Calculations made with the Equilibrium Module of Ref. [2] show that the 600°C maximum temperature specified for this reaction is adequate, but the O2 yield could be increased from 1.860 mole to 1.970 mole by increasing the temperature to 1540°C.

REACTION 126B

Reference [2] does not list CsHg amalgam in the database, so Cs + Hg were entered into the equation for Reaction 126B. **This calculation indicated that reaction 126B is nonspontaneous from 0 to 3000°C.**

REACTION 126C

Because CsHg amalgam is not listed in the database, Cs + Hg were entered into the equation for Reaction 126C. This calculation indicated that the equilibrium for reaction 126C lies to the

right at temperatures up to 2913°C. The maximum temperature for this reaction is not specified in the Ref. [1] database, but can be calculated with the Equilibrium Module to determine the optimum temperature for reaction product yield and separability.

REACTION 126D

Calculations made with Ref. [2] show that reaction 126D is nonspontaneous at temperatures from 0 to 3000°C.

SUMMARY

Because reactions 126B and 126D are nonspontaneous at all temperatures between 0 and 3000°C, PID 126 is not workable as presented in the UNLV database, and further evaluation of this cycle is unnecessary.

A copy of this cycle from Ref. [1] is shown below along with delta G calculations for reactions 126B and 126D.

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

REACTION 126B (Reaction Code CsO x 2) DELTA G CALCULATION FROM REF. 2

-

$2CsO2 + 6Hg = 2Cs + 2Hg + 4HgO$

T	deltaH	deltaS	deltaG	K	Log(K)
C	kJ	J/K	kJ		
0.000	209.703	-134.175	246.353	7.689E-048	-47.114
100.000	211.143	-128.978	259.272	5.051E-037	-36.297
200.000	209.130	-133.774	272.426	8.363E-031	-30.078
300.000	207.307	-137.273	285.985	8.596E-027	-26.066
400.000	205.513	-140.158	299.860	5.367E-024	-23.270
500.000	203.702	-142.666	314.004	6.080E-022	-21.216
600.000	201.895	-144.864	328.383	2.257E-020	-19.647
700.000	200.144	-146.764	342.967	3.885E-019	-18.411
800.000	198.525	-148.349	357.725	3.860E-018	-17.413
900.000	197.125	-149.598	372.625	2.555E-017	-16.593
1000.000	196.033	-150.492	387.633	1.244E-016	-15.905
1100.000	195.343	-151.016	402.712	4.782E-016	-15.320
1200.000	195.148	-151.156	417.823	1.526E-015	-14.816
1300.000	195.543	-150.899	432.930	4.206E-015	-14.376
1400.000	196.622	-150.236	447.990	1.030E-014	-13.987
1500.000	198.483	-149.158	462.963	2.294E-014	-13.639
1600.000	201.221	-147.658	477.807	4.729E-014	-13.325
1700.000	204.934	-145.730	492.480	9.154E-014	-13.038
1800.000	209.718	-143.367	506.939	1.684E-013	-12.774
1900.000	215.670	-140.565	521.139	2.969E-013	-12.527
2000.000	222.887	-137.320	535.037	5.063E-013	-12.296
2100.000	231.468	-133.628	548.588	8.398E-013	-12.076
2200.000	241.508	-129.487	561.748	1.363E-012	-11.865
2300.000	253.106	-124.891	574.470	2.174E-012	-11.663
2400.000	266.359	-119.840	586.711	3.423E-012	-11.466
2500.000	281.365	-114.331	598.423	5.336E-012	-11.273
2600.000	298.221	-108.362	609.562	8.262E-012	-11.083
2700.000	317.025	-101.931	620.080	1.274E-011	-10.895
2800.000	337.874	-95.036	629.932	1.959E-011	-10.708
2900.000	360.866	-87.675	639.072	3.014E-011	-10.521
3000.000	386.099	-79.847	647.452	4.643E-011	-10.333

CsO2	Extrapolated from	830.000	K	
Hg	Extrapolated from	2000.000	K	
Cs	Extrapolated from	2000.000	K	
Hg	Extrapolated from	2000.000	K	
HgO	Extrapolated from	1500.000	K	

Formula	FM	Conc. Amount	Amount	Volume

	g/mol	wt-%	mol	g	l or ml	
CsO2	164.904	21.509	2.000	329.808	87.482	ml
Hg	200.590	78.491	6.000	1203.540	88.930	ml
	g/mol	wt-%	mol	g	l or ml	
Cs	132.905	17.335	2.000	265.811	137.726	ml
Hg	200.590	26.164	2.000	401.180	29.643	ml
HgO	216.589	56.501	4.000	866.358	77.770	ml

REACTION CSOH-1 (Reaction Code 126D x 2) DELTA G CALCULATION FROM REF. 2 -

Reaction CsOH-1; (H2O = gas)

4CsOH + 3O2(g) = 4CsO2 +2 H2O(g)
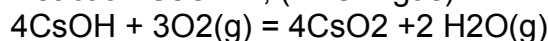
T	deltaH	deltaS	deltaG	K	Log(K)
C	kJ	J/K	kJ		
0.000	36.045	-86.886	59.778	3.696E-012	-11.432
100.000	37.546	-82.200	68.219	2.816E-010	-9.550
200.000	38.364	-80.221	76.320	3.748E-009	-8.426
300.000	19.254	-118.907	87.405	1.080E-008	-7.966
400.000	2.344	-147.680	101.754	1.269E-008	-7.897
500.000	2.827	-147.030	116.503	1.344E-008	-7.872
600.000	4.571	-144.925	131.112	1.432E-008	-7.844
700.000	7.619	-141.633	145.449	1.557E-008	-7.808
800.000	12.003	-137.355	159.406	1.739E-008	-7.760
900.000	17.752	-132.242	172.892	2.001E-008	-7.699
1000.000	24.881	-126.419	185.831	2.372E-008	-7.625
1100.000	33.381	-119.998	198.156	2.894E-008	-7.538
1200.000	43.243	-113.071	209.813	3.630E-008	-7.440
1300.000	54.459	-105.709	220.756	4.671E-008	-7.331
1400.000	67.018	-97.974	230.943	6.159E-008	-7.210
1500.000	80.912	-89.912	240.340	8.305E-008	-7.081
1600.000	96.132	-81.565	248.916	1.143E-007	-6.942
1700.000	112.669	-72.967	256.644	1.605E-007	-6.795
1800.000	130.515	-64.147	263.502	2.293E-007	-6.640
1900.000	149.661	-55.130	269.467	3.330E-007	-6.478
2000.000	170.099	-45.937	274.522	4.912E-007	-6.309
2100.000	191.820	-36.588	278.649	7.349E-007	-6.134
2200.000	214.815	-27.099	281.835	1.114E-006	-5.953
2300.000	239.078	-17.483	284.065	1.710E-006	-5.767
2400.000	264.602	-7.753	285.328	2.655E-006	-5.576
2500.000	291.381	2.080	285.612	4.167E-006	-5.380
2600.000	319.408	12.008	284.908	6.605E-006	-5.180
2700.000	348.685	22.023	283.208	1.057E-005	-4.976
2800.000	379.210	32.120	280.501	1.706E-005	-4.768
2900.000	410.982	42.293	276.781	2.776E-005	-4.557
3000.000	444.002	52.537	272.040	4.553E-005	-4.342

CsOH   Extrapolated from   2000.000   K
CsO2   Extrapolated from   830.000   K

Formula	FM	Conc.	Amount		Amount	Volume	
	g/mol	wt-%	mol	g	l or ml		
CsOH	149.913	86.200	4.000	599.651		163.170	ml
O2(g)	31.999	13.800	3.000	95.996		67.241	l
	g/mol	wt-%	mol	g	l or ml		
CsO2	164.904	94.821	4.000	659.617		174.965	ml
H2O(g)	18.015		5.179	2.000	36.030	44.827	l

Reaction CsOH-1 (Reaction Code 126D x 2)
$4CsOH + 3O_2(g) = 4CsO_2 + 2H_2O$
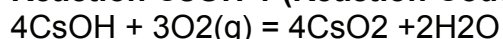
T	deltaH	deltaS	deltaG	K	Log(K)
C	kJ	J/K	kJ		
0.000	-66.050	-375.895	36.626	9.897E-008	-7.005
100.000	-44.199	-301.230	68.205	2.829E-010	-9.548
200.000	-34.668	-278.601	97.152	1.878E-011	-10.726
300.000	-43.131	-296.978	127.083	2.614E-012	-11.583
400.000	-44.407	-300.660	157.982	5.495E-013	-12.260
500.000	-28.016	-277.973	186.899	2.355E-013	-12.628
600.000	-10.614	-256.819	213.627	1.656E-013	-12.781
700.000	7.839	-236.821	238.301	1.614E-013	-12.792
800.000	27.369	-217.726	261.022	1.968E-013	-12.706
900.000	48.002	-199.350	281.870	2.810E-013	-12.551
1000.000	69.756	-181.561	300.911	4.500E-013	-12.347
1100.000	92.645	-164.260	318.199	7.847E-013	-12.105
1200.000	116.675	-147.373	333.777	1.459E-012	-11.836
1300.000	141.853	-130.841	347.685	2.848E-012	-11.545
1400.000	168.182	-114.618	359.956	5.774E-012	-11.239
1500.000	195.666	-98.667	370.618	1.206E-011	-10.919
1600.000	224.305	-82.958	379.697	2.576E-011	-10.589
1700.000	254.101	-67.464	387.216	5.604E-011	-10.252
1800.000	285.055	-52.163	393.196	1.237E-010	-9.908
1900.000	317.168	-37.037	397.655	2.761E-010	-9.559
2000.000	350.440	-22.070	400.609	6.218E-010	-9.206
2100.000	384.871	-7.249	402.074	1.410E-009	-8.851
2200.000	420.460	7.439	402.063	3.217E-009	-8.493
2300.000	457.211	22.004	400.590	7.369E-009	-8.133
2400.000	495.123	36.458	397.666	1.693E-008	-7.771
2500.000	534.197	50.807	393.302	3.901E-008	-7.409
2600.000	574.436	65.060	387.508	9.004E-008	-7.046
2700.000	615.841	79.225	380.293	2.080E-007	-6.682
2800.000	658.413	93.307	371.666	4.811E-007	-6.318
2900.000	702.156	107.314	361.634	1.113E-006	-5.954

3000.000   747.069   121.248   350.205   2.575E-006 -5.589

CsOH   Extrapolated from   2000.000   K
CsO2   Extrapolated from   830.000   K
H2O   Extrapolated from   610.000   K

Formula	FM	Conc.	Amount	Amount	Volume	
	g/mol	wt-%	mol g	l or ml		
CsOH	149.913	86.200	4.000 599.651		163.170	ml
O2(g)	31.999	13.800	3.000 95.996		67.241	l
	g/mol	wt-%	mol g	l or ml		
CsO2	164.904	94.821	4.000 659.617		174.965	ml
H2O	18.015	5.179	2.000 36.030	39.292	ml	

Reaction 126D (Reaction Code CsOH-1 x 0.5)

2CsOH + 1.5O2(g) = 2CsO2 + H2O
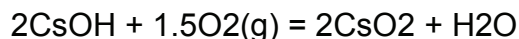
T	deltaH	deltaS	deltaG	K	Log(K)
C	kJ	J/K	kJ		
0.000	-33.025	-187.947	18.313	3.146E-004	-3.502
100.000	-22.100	-150.615	34.102	1.682E-005	-4.774
200.000	-17.334	-139.301	48.576	4.334E-006	-5.363
300.000	-21.565	-148.489	63.541	1.617E-006	-5.791
400.000	-22.204	-150.330	78.991	7.413E-007	-6.130
500.000	-14.008	-138.987	93.449	4.852E-007	-6.314
600.000	-5.307	-128.409	106.814	4.069E-007	-6.390
700.000	3.919	-118.411	119.151	4.018E-007	-6.396
800.000	13.685	-108.863	130.511	4.436E-007	-6.353
900.000	24.001	-99.675	140.935	5.301E-007	-6.276
1000.000	34.878	-90.781	150.456	6.708E-007	-6.173
1100.000	46.322	-82.130	159.099	8.858E-007	-6.053
1200.000	58.338	-73.686	166.889	1.208E-006	-5.918
1300.000	70.927	-65.420	173.843	1.688E-006	-5.773
1400.000	84.091	-57.309	179.978	2.403E-006	-5.619
1500.000	97.833	-49.334	185.309	3.472E-006	-5.459
1600.000	112.152	-41.479	189.849	5.075E-006	-5.295
1700.000	127.050	-33.732	193.608	7.486E-006	-5.126
1800.000	142.527	-26.081	196.598	1.112E-005	-4.954
1900.000	158.584	-18.518	198.827	1.662E-005	-4.779
2000.000	175.220	-11.035	200.304	2.494E-005	-4.603
2100.000	192.435	-3.625	201.037	3.756E-005	-4.425
2200.000	210.230	3.719	201.032	5.672E-005	-4.246
2300.000	228.605	11.002	200.295	8.584E-005	-4.066
2400.000	247.561	18.229	198.833	1.301E-004	-3.886
2500.000	267.098	25.403	196.651	1.975E-004	-3.704
2600.000	287.218	32.530	193.754	3.001E-004	-3.523

2700.000	307.920	39.612	190.146	4.561E-004	-3.341
2800.000	329.207	46.654	185.833	6.936E-004	-3.159
2900.000	351.078	53.657	180.817	1.055E-003	-2.977
3000.000	373.535	60.624	175.103	1.605E-003	-2.795

CsOH	Extrapolated from		2000.000	K
CsO2	Extrapolated from		830.000	K
H2O	Extrapolated from		610.000	K

Formula	FM	Conc.	Amount	Amount	Volume	
	g/mol	wt-%	mol	g	l or ml	
CsOH	149.913	86.200	2.000	299.825	81.585	ml
O2(g)	31.999	13.800	1.500	47.998	33.620	l
	g/mol	wt-%	mol	g	l or ml	
CsO2	164.904	94.821	2.000	329.808	87.482	ml
H2O	18.015	5.179	1.000	18.015	19.646	ml

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PID 129 – MAGNESIUM SULFATE

This process is based on the following chemical reactions from Ref. [1]:

Reaction No.	Reaction Code	Formula	Multiplier	Max. Temp. (˚C)
129A	MgSO4-1	MgSO4(s) = MgO(s) + SO2 + ½ O2	1.0	995
129B	MgO-3	MgO(s) + SO2 + H2O(l) = MgSO4(s) + H2	1.0	50

SUMMARY

Thermodynamically, reaction 129B is not the most favored. If the reaction 129B product mix could be achieved, the efficiency would approach 62.1%. If the favored equilibrium product mix is formed, however, the maximum efficiency is 6%. At this low efficiency, PID 129 is not a viable candidate for commercial hydrogen production.

Discussions of each reaction along with the equilibrium pictures for reactions 129A (Fig. 1) and 129B (Fig. 2) and the input data for these calculations (Tables 1 & 2) are shown below.
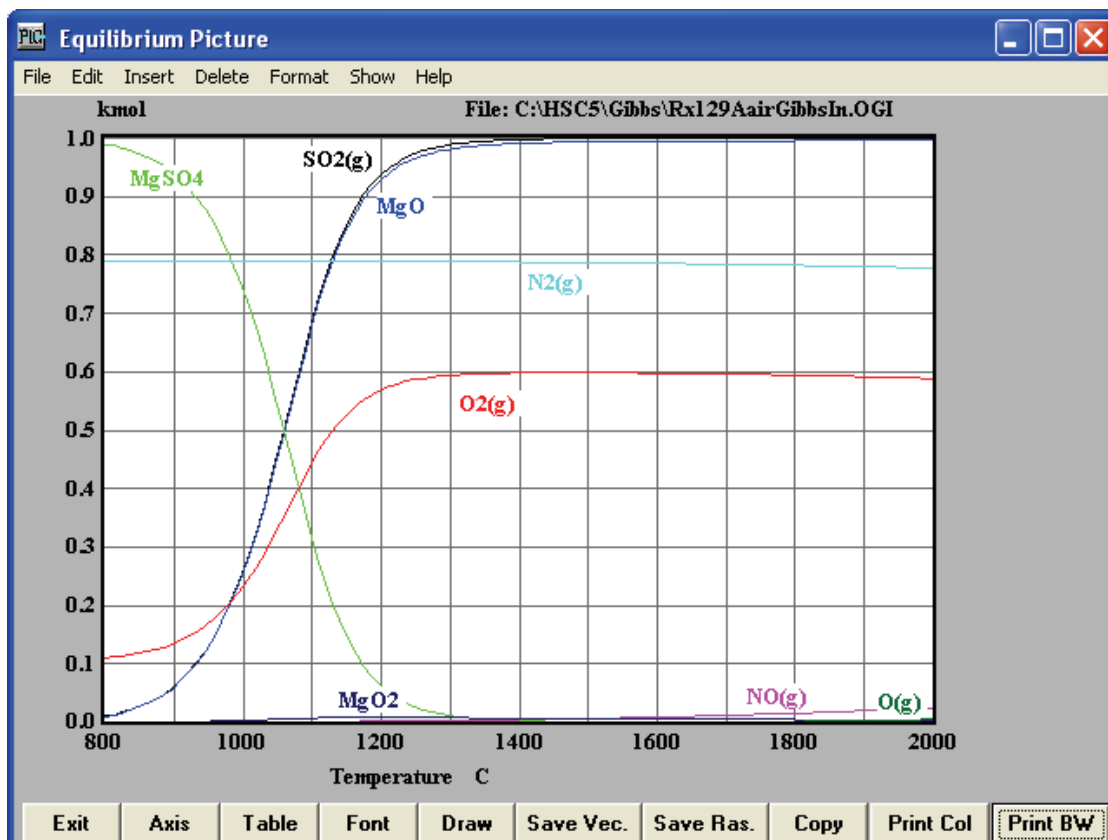
Fig. 1. Reaction 129A equilibrium picture. Reaction 129A, MgSO4 = MgO + SO2(g) + 0.5(g).

Table 1. Reaction 129a equilibrium calculation input data. Reaction 129A — MgSO4 = MgO + SO2(g) + 0.5 O2(g).

	A	B	C	D	E	F	G
	Equilibrium Calculations C:\HSC5\Gibbs\Rx129AairGibbsIn.igi						
	File Edit View Insert Delete Format Units Calculate Help						
	A1						
1							
2	File Format:		GIBBS		C:\HSC5\Gibbs\Rx129AairGibbsIn.igi		
3	Pure Substances in the Last Phase		NO				
4	Increase Temperature	100	Steps		Criss-Cobble On		
5	Temperature Range:	800.000	2000.000	C			
6	Pressure Range:	1.000	1.000	bar			
7							
8	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
9	GASES		1.000	100.000			
10	Mg(g)	25.000					1.000
11	Mg2(g)	25.000					1.000
12	MgO(g)	25.000					1.000
13	N2(g)	25.000	0.790	79.000			1.000
14	NO(g)	25.000					1.000
15	NO2(g)	25.000					1.000
16	NO3(g)	25.000					1.000
17	O(g)	25.000	0.210	21.000			1.000
18	O2(g)	25.000					1.000
19	SO2(g)	25.000					1.000
20	OXIDES, etc.		1.000	100.000			
21	MgO	25.000					1.000
22	MgO2	25.000					1.000
23	MgSO3	25.000					1.000
24	MgSO4	25.000	1.000	100.000			1.000
25	ELEMENTS						
26	Mg	25.000					1.000
27							

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REACTION 129A

Calculations made with the Ref. [2] program show that reaction 129A is spontaneous at temperatures above 1145°C, where delta G is zero. The 995°C maximum temperature specified for this reaction is too low, and should be increased to at least 1400°C for the reaction to proceed at an acceptable rate with maximum production of MgO and SO2 (see the equilibrium picture in Fig. 1 and input calculations in Table 1 below). An air purge preheated to 1390 °C would be provided to sweep the SO2/O2 offgas mixture from Reactor 129A into the SO2 separation system. The purge air would be preheated by the hot MgO exiting Reactor 129A. The Reactor 129A offgas mixture would be cooled to 40°C in Offgas Cooler 129A.

Table 2. Reaction 129b equilibrium calculation input data. Reaction 129B (H2 yield = 0.106 mole maximum). Primary reaction: MgO + SO2(g) + H2O(l) = MgSO3 + H2O(g) (No H2 production). Secondary reaction: MgO + SO2(g) + H2O(l) = MgSO4 + H2(g) (Reaction Code MgO-3)

Equilibrium Calculations C:\HSC5\Gibbs\Rx129BGibbsIn.igi

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A1

	A	B	C	D	E	F	G
1							
2	File Format:		GIBBS		C:\HSC5\Gibbs\Rx129BGibbsIn.igi		
3	Pure Substances in the Last Phase		NO				
4	Increase Temperature	100	Steps		Criss-Cobble On		
5	Temperature Range:	0.000	500.000	C			
6	Pressure Range:	1.000	1.000	bar			
7							
8	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
9	GASES		2.000	100.000			
10	H(g)	25.000					1.000
11	H2(g)	25.000					1.000
12	H2O(g)	25.000	1.000	50.000			1.000
13	Mg(g)	25.000					1.000
14	Mg2(g)	25.000					1.000
15	MgO(g)	25.000					1.000
16	O(g)	25.000					1.000
17	O2(g)	25.000					1.000
18	SO2(g)	25.000	1.000	50.000			1.000
19	OXIDES, etc.		1.000	100.000			
20	H2O	25.000					1.000
21	MgO	25.000	1.000	100.000			1.000
22	MgO2	25.000					1.000
23	MgSO3	25.000					1.000
24	MgSO4	25.000					1.000
25	ELEMENTS						
26	Mg	25.000					1.000
27							
28							
29							

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Exit   Ins Phase   Del Phase   Ins Row   Del Row   Open   \HSC5\Gibbs\Rx129BGibbsIn.i   Save   Gibbs

Following cooling, gases from Reactor 129A would be compressed and chilled to liquefy and separate the SO2. The O2/air product stream would then be scrubbed with feed H2O before it is discharged from the system.

REACTION 129B

Note that the favored product for reaction 129B is MgSO3 (not MgSO4) with a maximum H2 yield of 10% at 400°C. Confirming calculations using the Equilibrium Module of Ref. [2] verify these values (see the equilibrium picture in Fig. 2 and input calculations in Table 2 below). Under these assumptions, the calculated efficiency for this cycle of only 6%.
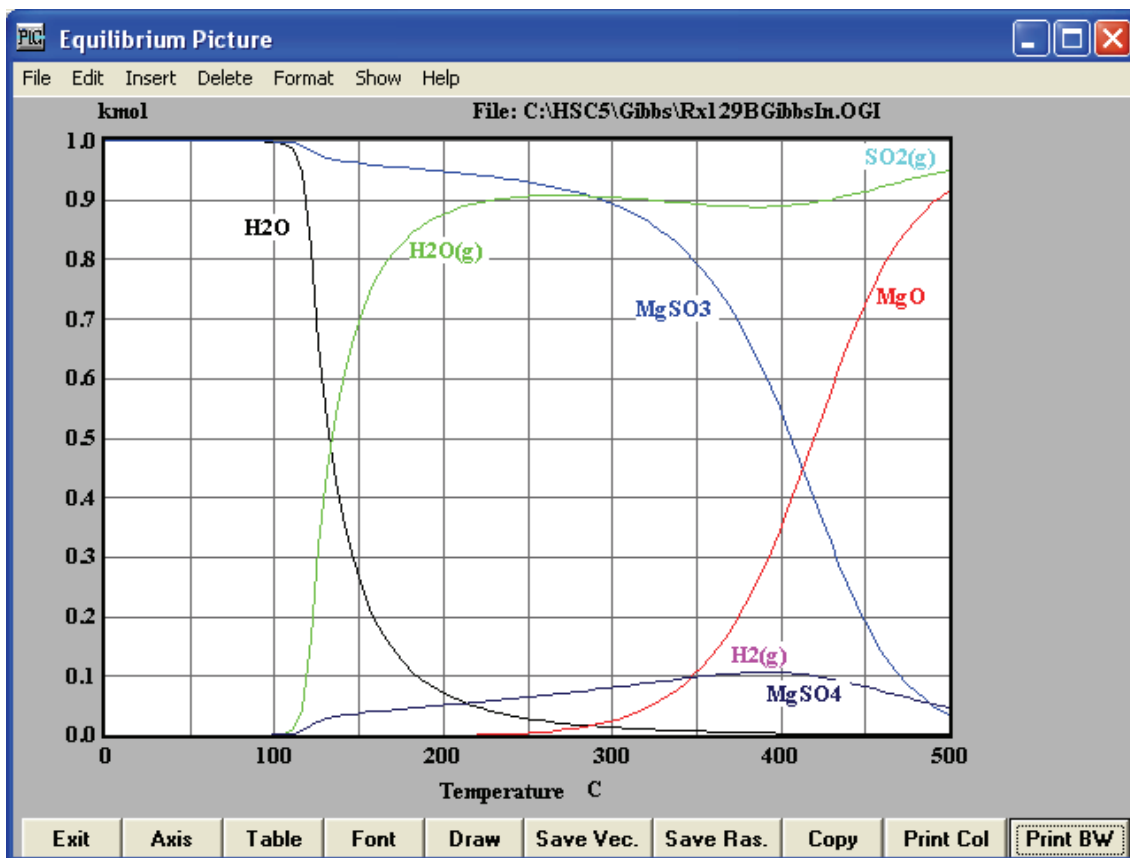
Fig. 2. Reaction 129B equilibrium picture. Reaction 129B (H2 yield = 0.106 mole maximum). Primary reaction: MgO + SO2(g) + H2O(I) = MgS03 + H2O(g) (No H2 production). Secondary reaction: MgO + SO2(g) + H2O(I) = MgS04 + H2(g) (reasction code MgO-3).

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

PID 131 – MANGANESE SULFATE

This cycle is based on the following chemical reactions from Ref. 1:

Reaction No.	Formula	Max. Temp. (°C)
131A	MnSO4 = MnO + SO2 + 0.5 O2	1100
131B	MnO + SO2 + H2O = MnSO4 + H2	0

SUMMARY

If the reaction 131A product mix specified above could be achieved, the efficiency of this cycle would approach 60.3%. Thermodynamic calculations, however, indicate that reaction 131A favors production of mixed oxides with a resulting decrease in H2 yield from reaction 131B. When this product mix is formed, the maximum efficiency decreases to 41.8%. This is sufficiently high to justify a more rigorous evaluation. Experimental data are also needed to quantify the kinetics and product yields of the reactions.

Discussions of each reaction along with a simplified flowsheet for this cycle (Fig. 1) are shown below.

REACTION 131A

Calculations made with the Ref. [2] program show that reaction 131A is spontaneous at temperatures above 1067°C, where delta G is zero. The reaction 131A product distribution, as calculated with the Equilibrium Module of Ref. 2, indicated production of Mn3O4, Mn2O2, MnO2 and SO3 in addition to the MnO and SO2. The 1100°C maximum temperature specified for Reactor 131A is adequate, but a 1500°C temperature was selected for this assessment to increase MnO and SO2 production while reducing the yield of the mixed oxides other than MnO (Fig. 2). The 1500°C recommended operating temperature in Reactor 131A can be maintained with a 442.54 MJ solar heater.

An air purge preheated to 1490°C is provided to sweep the SO2/SO3/O2 offgas mixture from Reactor 131A into the SO2/SO3 separation system. The purge air is preheated by the hot Mn oxides exiting Reactor 131A. The Reactor 131A offgas mixture is cooled to 40°C in Offgas Cooler 131A.

Following cooling, gases from Reactor 131A are compressed and chilled to liquefy and separate the SO2 and SO3. The O2/air product stream is scrubbed with feed H2O before it is discharged from the system. The liquid SO2 and solid SO3 are fed along with the Mn oxides from Reactor 131A and H2O from the scrubbers into Reactor 131B.

Scrubber 131A

O2/Air (g) Product ③·¹

H₂O(l) ①·³

H2(g) Product

Scrubber 131B

H₂O Feed ①·²   ②·²

O2/Air(g) ③

Condenser 131A
Duty= -29.12 MJ
Pressure = 2.39 bar
Power = 1.72 kW
Heat eq. = 16.27 MJ

SO2(l) ⑤

①

H₂O Feed

H₂O

Gas Compressor 131A
4 kW = 37.9 MJ Heat eq.

④·²

④·¹

SO2(g) + O2(g)

Offgas Cooler 131A
Total Duty = -145.56 MJ
-80.99 MJ Recovered in
Heater 131B

H2(g) ②·¹

H2 Cooler 131B
-1.99 MJ

Cooler 131B
Duty = -120.74 MJ

②

①·¹

④

REACTOR 131A

MnSO4 =
Mnₓ O y + SO2 + SO3 + O2
dG = 0 at 1067°C

T = 1500°C

MnₓOy

⑥

REACTOR 131B

Mnₓ O y + SO2 + SO3 + H2O =
MnSO4*H₂O + H2
dG = 0 at 290°C

T = 120°C

MnSO4*xH₂O
m.p. = 700°C

⑥·¹

⑦

Solar Heater 131A
Duty = 442.54 MJ

⑦·¹ MnSO4

Purge Air

Air Preheater 131A, Duty = 48.23 MJ

⑧·¹

Purge Air ⑧

H2O

⑦·¹

MnSO4 Heater/Dryer 131B
Total Duty = 93.37 MJ, all
recovered from Offgas
Cooler 131A

MnSO4(l) ⑦·²

System Thermal Efficiency =   41.8%

Fig. 1. Solar hydrogen generation project, PID 131 flowsheet, Rev. 1.

A2-109
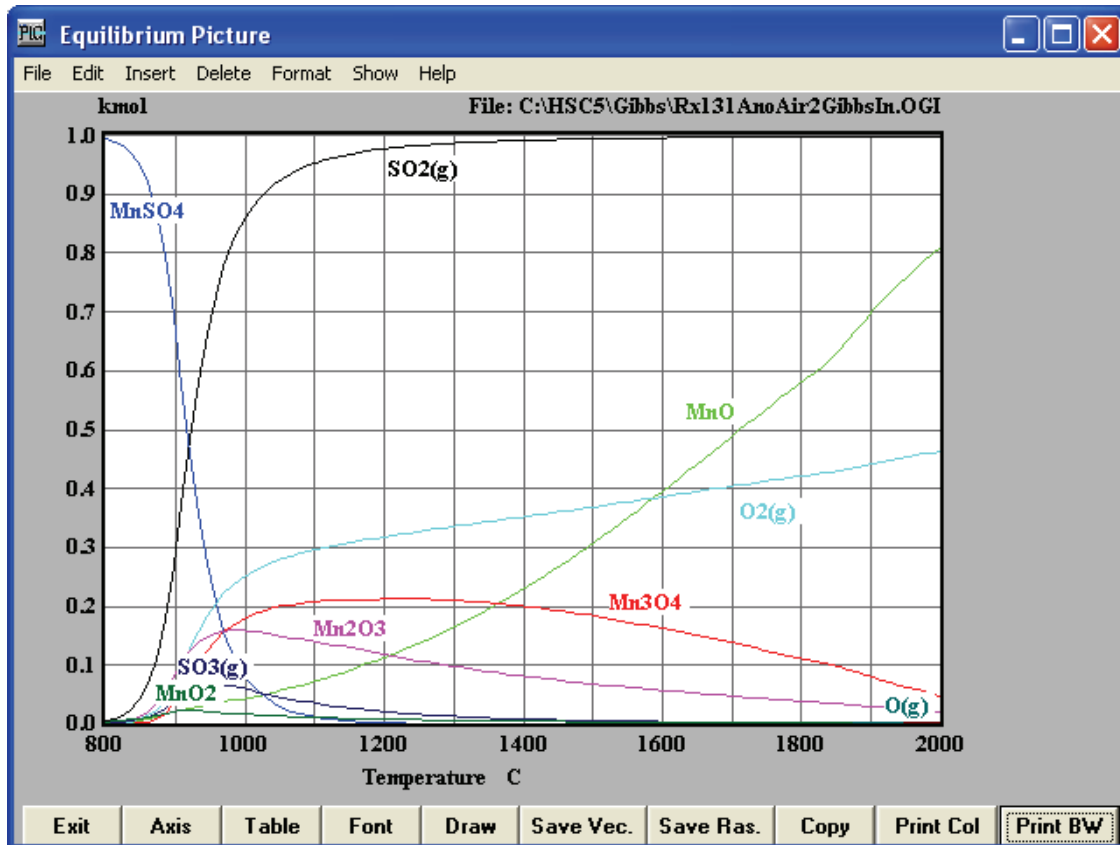
Fig. 2. Reaction 131a equilibrium picture.

REACTION 131B

The equilibrium for reaction 131B lies to the right at temperatures below 290°C. A 120°C temperature was selected for this assessment, because it increases H2 production and vaporizes the water before the MnSO4 and MnSO4*H2O are transferred to Heater/Dryer 131B. Heater/Dryer 131B recovers 93.37 MJ from Offgas Cooler 131A to increase the MnSO4 temperature to 600°C before it is transferred to reactor 131A. The formation of sulfides was not included in the equilibrium calculations because the kinetics for their formation is slow.

As a result of the mixed oxide production in reaction 131A, the H2 yield is reduced from the theoretical 1 mole to 0.726 mole. The corresponding thermal efficiency of this cycle is reduced from 60.3% to 41.8%.

The exotherm from reaction 131B together with the heat content in the reactants requires a 120.74 MJ cooler to maintain 120°C in the reactor. The H2 product is cooled to 25°C in H2 Cooler 131B with a heat rejection of 1.99 MJ, and scrubbed with feed water before it is discharged to storage.

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows", Version 5.11 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 200

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 132 – FERROUS SULFATE-3

This process is based on the following chemical reactions from Ref. [1]:

Reaction No.	Formula	Max. Temp. ($^\circ$C)
132A	FeSO4(s) = FeO(s) + SO2 + 1/2 O2	1100
132B	FeO(s) + SO2 + H2O = FeSO4(s) + H2	0

SUMMARY

Thermodynamic calculations show that the primary products of reaction 132A are Fe2O3, Fe3O4, SO2 and O2. After the O2 is separated, Fe2O3, Fe3O4, SO2 are added with H2O to reactor 132B to produce 0.5 mole H2. The estimated efficiency for this cycle is 17%. This low yield indicates that PID 132 is not a viable candidate for commercial hydrogen production. This efficiency calculation assumes that the H2 product can be removed from the process before it enters side reactions that could form FeS, H2S, or S.

REACTION 132A

Reaction 132A (Ref. [1] Reaction Code FeSO4-2) specifies that FeSO4 decomposition will produce FeO and SO2 as reaction products. Thermodynamic calculations as shown in the equilibrium picture (Fig. 1 and Table 1), however, indicate that the products of this reaction are Fe2O3, Fe3O4, SO2 and O2.

REACTION 132B

The equilibrium for reaction 132B lies to the right at temperatures below 235°C. When the equilibrium mixture of Fe oxides and SO2 from reaction 132A are added with H2O to reactor 132B, a maximum 0.51 mole H2 is produced. This low yield decreases the estimated efficiency from the theoretical value of 34% to 17% at an operating temperature of 50°C (Fig. 2 & Table 2). These values were also calculated for an aqueous reaction with the same results (Fig. 3 & Table 3). These efficiency calculations assume that the H2 can be removed from the process before it enters side reactions that could form FeS, H2S, or S.

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

Fig. 1. Reaction 132a equilibrium picture. Reaction 132A. FeS04 = FeO + SO2(g) + 0.502(g).

Table 1. Reaction 132A equilibrium calculation input

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6	Pressure Range:	1.000	1.000	bar			
7							
8	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
9	PHASE 1:						
10	Fe(g)	25.000					1.000
11	Fe2(g)	25.000					1.000
12	FeO(g)	25.000					1.000
13	FeO2(g)	25.000					1.000
14	FeS(g)	25.000					1.000
15	O2(g)	25.000					1.000
16	SO(g)	25.000					1.000
17	SO2(g)	25.000					1.000
18	SO3(g)	25.000					1.000
19	PHASE 2:		1.000	100.000			
20	FeO	25.000					1.000
21	Fe2O3	25.000					1.000
22	Fe3O4	25.000					1.000
23	FeSO4	25.000	1.000	100.000			1.000
24							
25							

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Fig. 2. Reaction 132b equilibrium picture. Reaction 132B. Specified Input: FeO + SO2(g) + H2O(g) = FeSO4 + H2(g). Actual input from Rx 132A + H2O: 0.360Fe2O3 + 0.092Fe3O3 + + 0.092Fe3O4 + 0.003FeO + 0.966SO2 + 0.034SO3 + H2O

Table 2. Reaction 132B equilibrium calculation input
Reaction 132B
Actual input from Rx 132A + H2O: $0.360Fe_2O_3 + 0.092Fe_3O_3 + + 0.092Fe_3O_4 + 0.003FeO + 0.966SO_2 + 0.034SO_3 + H_2O$

Equilibrium Calculations C:\HSC5\Gibbs\Rx132Arev1GibbsIn.igi

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A1

	A	B	C	D	E	F	G
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2	File Format:		GIBBS		C:\HSC5\Gibbs\Rx132Arev1GibbsIn.igi		
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4	Increase Temperature	101	Steps		Criss-Cobble On		
5	Temperature Range:	0.000	250.000	C			
6	Pressure Range:	1.000	1.000	bar			
7							
8	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
9	GASES		1.000	100.000			
10	H2(g)	25.000					1.000
11	H2O(g)	25.000					1.000
12	O2(g)	25.000					1.000
13	SO2(g)	25.000	0.966	96.600			1.000
14	SO3(g)	25.000	0.034	3.400			1.000
15	OXIDES, etc.		1.455	100.000			
16	FeO	25.000	0.003	0.206			1.000
17	Fe2O3	25.000	0.360	24.742			1.000
18	Fe3O4	25.000	0.092	6.323			1.000
19	Fe2O3*H2O	25.000					1.000
20	FeO*OH	25.000					1.000
21	FeSO4	25.000					1.000
22	Fe2(SO4)3	25.000					1.000
23	FeSO4*H2O	25.000					1.000
24	FeSO4*4H2O	25.000					1.000
25	FeSO4*7H2O	25.000					1.000
26	H2O	25.000	1.000	68.729			1.000
27							
28							

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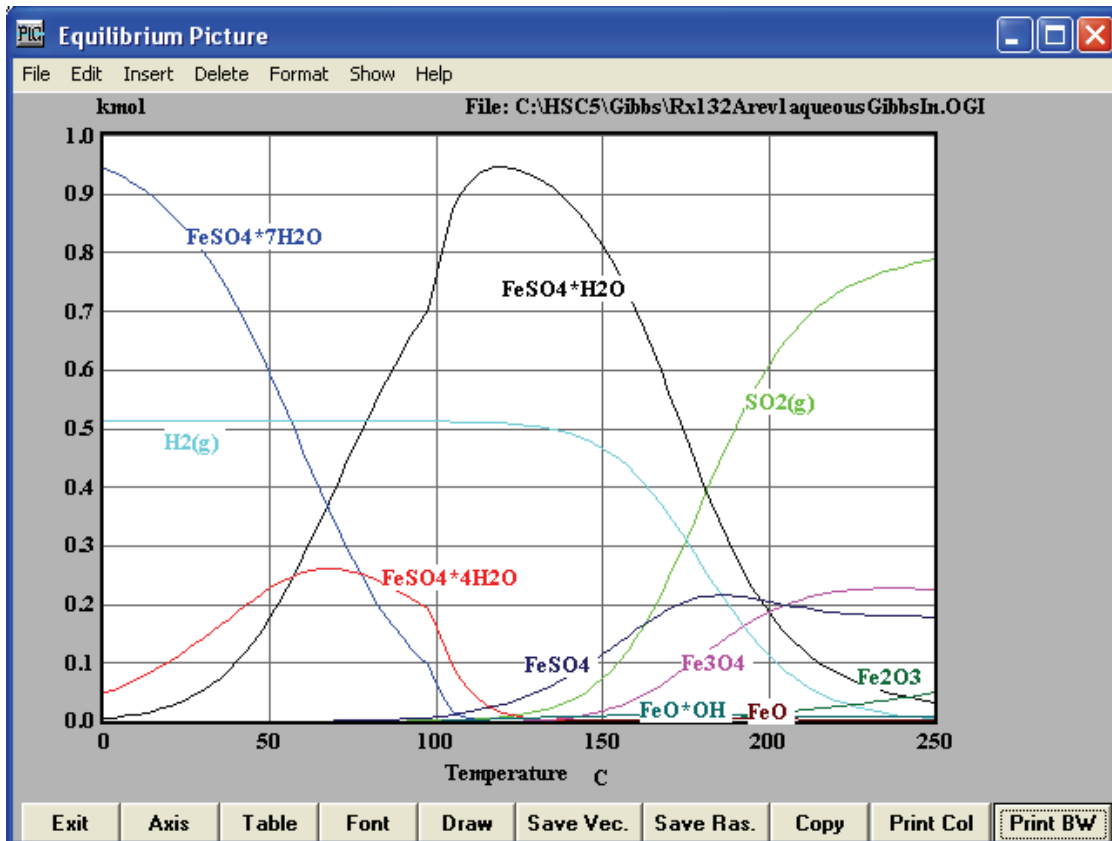
Fig. 3. Reaction 132B equilibrium picture – in aqueous solution.

Table 3. Reaction 132B equilibrium calculation input for an aqueous reactor

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	A	B	C	D	E	F	G
1							
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3	Pure Substances in the Last Phase		NO				
4	Increase Temperature	101	Steps		Criss-Cobble On		
5	Temperature Range:	0.000	250.000	C			
6	Pressure Range:	1.000	1.000	bar			
7							
8	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
9	GASES		1.000	100.000			
10	H2(g)	25.000					1.000
11	H2O(g)	25.000					1.000
12	O2(g)	25.000					1.000
13	SO2(g)	25.000	0.966	96.600			1.000
14	SO3(g)	25.000	0.034	3.400			1.000
15	OXIDES, etc.	25.000	0.455	100.000			
16	FeO	25.000	0.003	0.659			1.000
17	Fe2O3	25.000	0.360	79.121			1.000
18	Fe3O4	25.000	0.092	20.220			1.000
19	Fe2O3*H2O	25.000					1.000
20	FeO*OH	25.000					1.000
21	FeSO4	25.000					1.000
22	Fe2(SO4)3	25.000					1.000
23	FeSO4*H2O	25.000					1.000
24	FeSO4*4H2O	25.000					1.000
25	FeSO4*7H2O	25.000					1.000
26	AQUEOUS	25.000	10.000	100.000			
27	FeSO4(ia)	25.000					1.000
28	Fe2(SO4)3(ia)	25.000					1.000
29	H2O(l)	25.000	10.000	100.000			1.000
30							
31							

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PID 133 – FERROUS SULFATE-4

This process is based on the following chemical reactions from Ref. [1]:

Reaction No.	Formula	Max. Temp. (°C)
133A	Fe3O4(s) + 3SO3 = 3 FeSO4(s) + 0.5O2	800
133B	3FeSO4(s) = 3FeO(s) + 3SO3(g)	1100
133C	3FeO(s) + H2O = Fe3O4(s) + H2	550

COMMENTS FROM REF. 1

General Comments:

8/27/2004 (mcquillan) FeSO4-3 reaction does not have the thermodynamically stable products. Thermodynamically, 2FeO + SO3(g) → Fe2O3 + SO2(g) at all temperatures. (TC note: this reaction is noted herein as Reaction 133B)

SUMMARY

The primary products of reaction 133B, FeSO4 decomposition, are Fe2O3, SO2 and O2. The FeO specified as a reactant to produce H2 in Reaction 133C is not produced in significant quantities. **This indicates that PID 133 is not workable as presented in the UNLV database, and further evaluation of this cycle is unnecessary.**

REACTION 133A

Calculations using Ref. [2] show that reaction 133A (Ref. [1] Reaction Code Fe3O4-8) is spontaneous at temperatures below 810°C, where delta G is zero. The 800°C maximum temperature specified in Ref. [1] for this reaction is too high, and should be decreased to <400°C to achieve more favorable kinetics and reaction product equilibria.

REACTION 133B

Reaction 133B (Ref. [1] Reaction Code FeSO4-3) specifies that FeSO4 decomposition will produce FeO and SO3 as reaction products. Thermodynamic calculations as shown in the equilibrium picture (Fig. 1 and Table 1), and the comment above, however, indicate that the products of this reaction are Fe2O3, SO2 and O2. The FeO specified as a reactant to produce H2 in Reaction 133C is not produced in significant quantities.

REACTION 133C

Calculations using Ref. [2] show that reaction 133C (Ref. [1] Reaction Code FeO-3) is spontaneous at temperatures below 2269°C, where delta G is zero. When the equilibrium mixture

of Fe oxides from reaction 132A are added with H2O to reactor 132B, no H2 is produced (Fig. 2 and Table 2). This indicates that PID 133 is not workable as presented in the UNLV database, and further evaluation of this cycle is unnecessary. The 550°C maximum temperature specified in Ref. [1] for this reaction would be evaluated if the cycle were viable.

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.
[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.
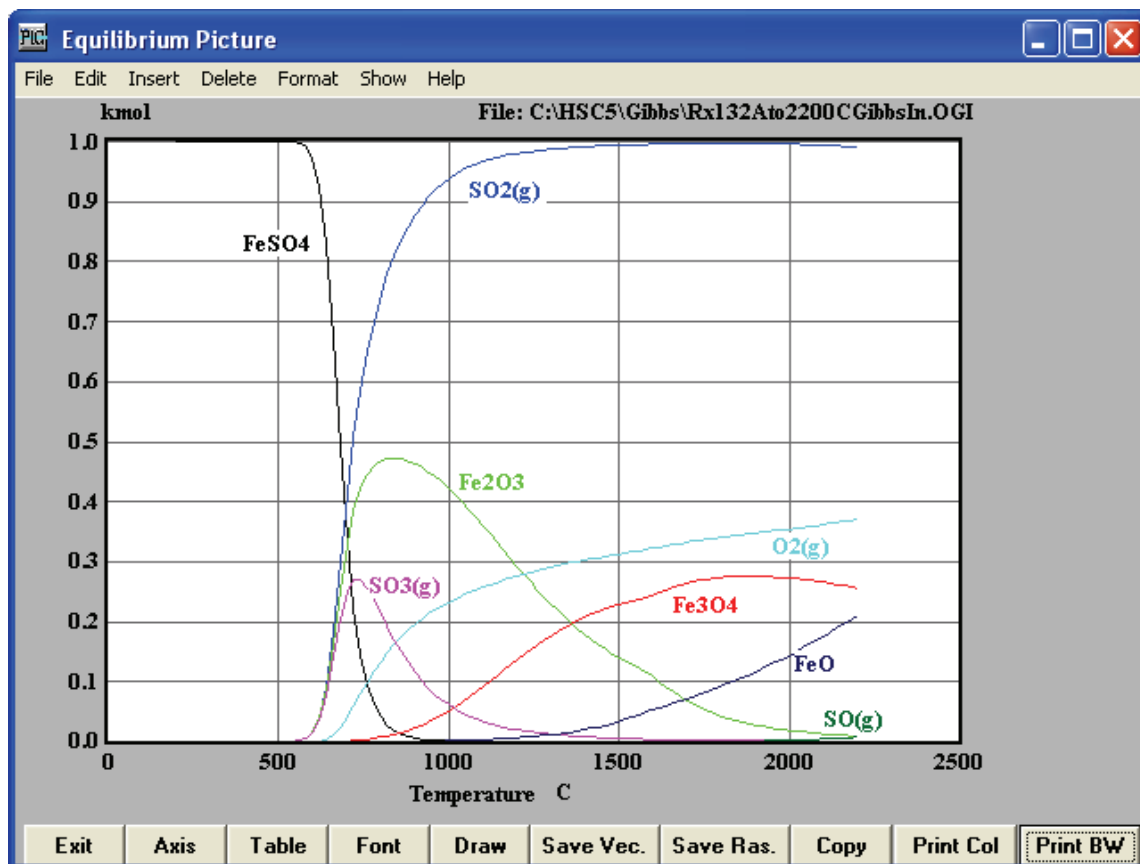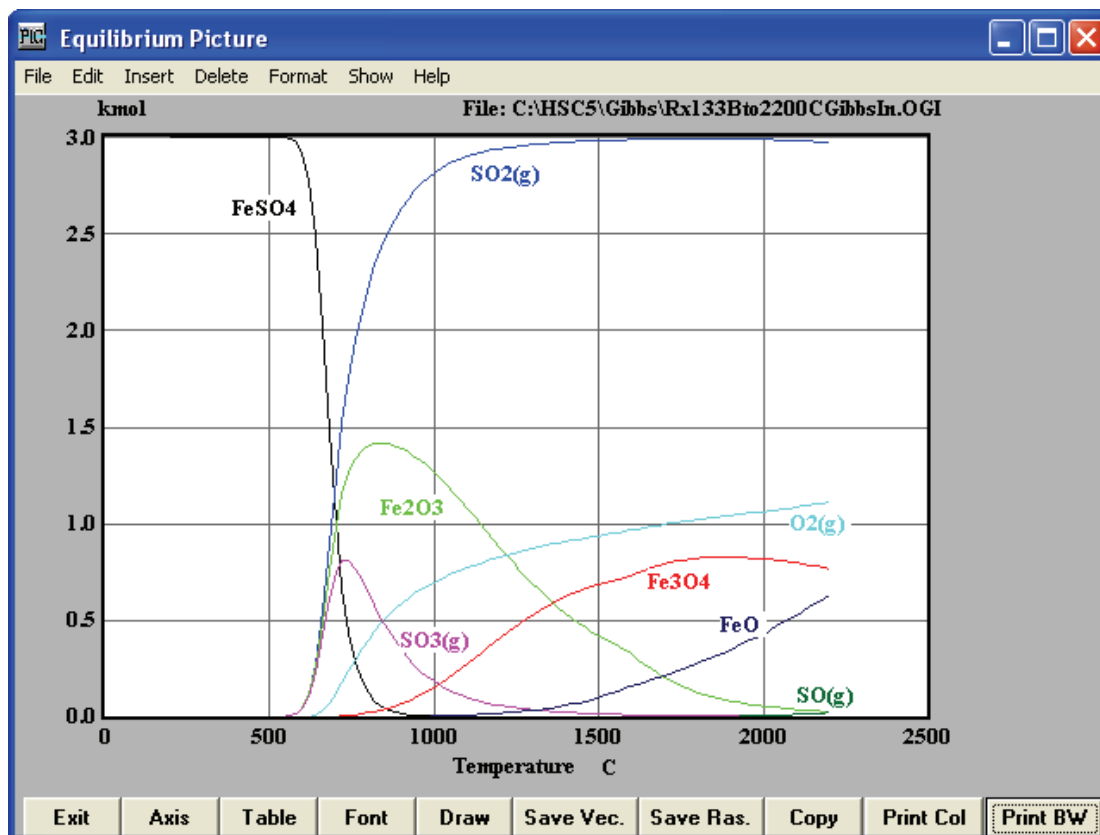
Fig. 1. Reaction 133B equilibrium picture.

Table 1. Reaction 133B Equilibrium Calculation Input.

	A	B	C	D	E	F	G
	Equilibrium Calculations C:\HSC5\Gibbs\Rx133Brev1GibbsIn.igi						
	File Edit View Insert Delete Format Units Calculate Help						
	A1						
1							
2	File Format:		GIBBS		C:\HSC5\Gibbs\Rx133Brev1GibbsIn.igi		
3	Pure Substances in the Last Phase		NO				
4	Increase Temperature	101	Steps		Criss-Cobble On		
5	Temperature Range:	200.000	2200.000	C			
6	Pressure Range:	1.000	1.000	bar			
7							
8	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
9	GASES						
10	FeO(g)	25.000					1.000
11	FeO2(g)	25.000					1.000
12	O2(g)	25.000					1.000
13	SO2(g)	25.000					1.000
14	SO3(g)	25.000					1.000
15	OXIDES, etc.		3.000	100.000			
16	FeO	25.000					1.000
17	Fe2O3	25.000					1.000
18	Fe3O4	25.000					1.000
19	FeSO4	25.000	3.000	100.000			1.000
20	ELEMENTS						
21	Fe	25.000					1.000
22							
23							
24							

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Exit | Ins Phase | Del Phase | Ins Row | Del Row | **Open** | HSC5\Gibbs\Rx133Brev1Gibbsl | **Save** | **Gibbs**

Fig. 2. Reaction 133C equilibrium picture.

Table 2. Reaction 133C Equilibrium Calculation Input.

	A	B	C	D	E	F	G
1							
2	File Format:		GIBBS		C:\HSC5\Gibbs\Rx133Crev1GibbsIn.igi		
3	Pure Substances in the Last Phase		NO				
4	Increase Temperature	121	Steps		Criss-Cobble On		
5	Temperature Range:	0.000	600.000	C			
6	Pressure Range:	1.000	1.000	bar			
7							
8	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
9	PHASE 1:						
10	H2(g)	25.000					1.000
11	H2O(g)	25.000					1.000
12	O2(g)	25.000					1.000
13	PHASE 2:		2.455	100.000			
14	FeO	25.000	0.100	4.073			1.000
15	Fe2O3	25.000	1.080	43.992			1.000
16	Fe3O4	25.000	0.275	11.202			1.000
17	Fe(OH)2	25.000					1.000
18	Fe(OH)3	25.000					1.000
19	Fe2O3*H2O	25.000					1.000
20	FeO*OH	25.000					1.000
21	H2O	25.000	1.000	40.733			1.000
22							

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 134 – COBALT SULFATE

This process is based on the following chemical reactions from Ref. [1]:

Reaction No.	Formula	Max. Temp. (°C)
134A	$CoSO_4(l) = CoO(s) + SO_2 + ½ O_2$	1100
134B	$CoO(s) + H_2O + SO_2 = CoSO_4(s) + H_2$	190

CONCLUSIONS

The maximum thermal efficiency from the PID 134 cycle is predicted to be 17.9%. This is sufficiently low to preclude further analysis of the cycle as presented in the Ref. [1] database. This efficiency calculation assumes that the H2 product can be removed from the process before it enters side reactions that could form CoS, H2S, or S.

REACTION 134A

Calculations using Ref. [2] show that reaction 134A is spontaneous at temperatures above 1006°C, where delta G is zero. The 1100°C maximum temperature selected for this reactor should be increased to 1500°C where O2 yield approaches a maximum 0.5 mole (Fig. 1 and Table 1). The 1500°C operating temperature can be maintained with a 489.58 MJ solar heater.

An air purge sweeps the SO2/O2 offgas mixture from the Reactor 134A into the SO2 separation system. The purge air is preheated by the hot CoO exiting Reactor 134A. The Reactor 134A offgas mixture is cooled to 40°C in Offgas Cooler 134A. Twenty eight percent of the heat from this cooler is recuperated in CoSO4 Dryer 134B. The 72% excess heat in Offgas Cooler 134A is rejected.

Following cooling, the gases are compressed and cooled in Condenser 134A to liquefy the SO2. The O2 is scrubbed with 0.333 mole feed H2O and removed with the air as product. The liquid SO2 is fed with the CoO from Reactor 134A and H2O from the scrubbers into reactor 134B.

REACTION 134B

The equilibrium for reaction 134B lies to the right at temperatures below 190°C. A 105°C temperature was selected to increase the H2 product yield to 0.341 mole (see Fig. 2 and Table 2), and to vaporize the feed water before the CoSO4•xH2O is transferred to Dryer 134B where the waters of crystallization are removed at 420°C, and the salt is dried at 440°C. Dryer 134B recovers 43.11 MJ from Offgas Cooler 134A to dry the CoSO4 and increase the temperature to 440°C. The CoSO4 is then transferred to reactor 134A.

Reaction 134A
CoSO4 =CoO + SO2(g) + 0.5O2(g)
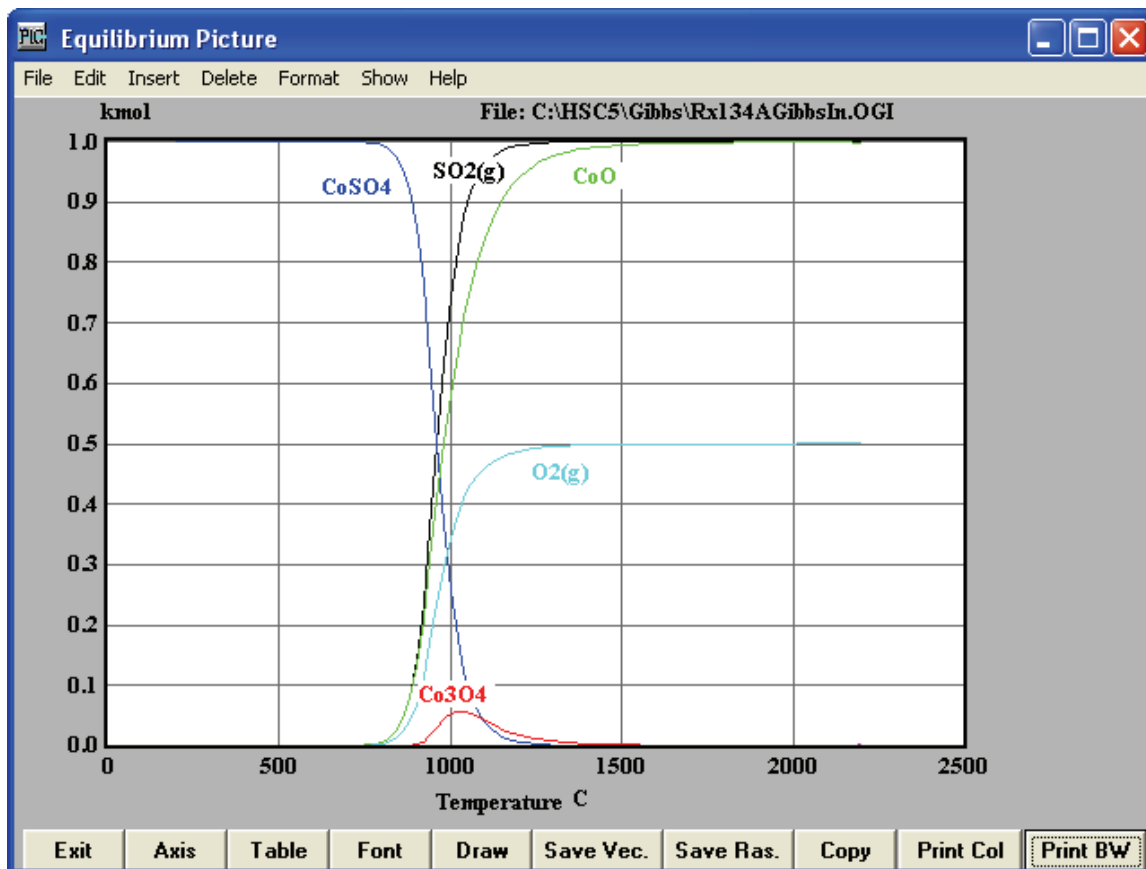
Fig. 1. Reaction 134A equilibrium picture.

Table 1. Reaction 134A equilibrium calculation input
Reaction 134A
CoSO4 =CoO + SO2(g) + 0.5O2(g)

Equilibrium Calculations C:\HSC5\Gibbs\Rx134AGibbsIn.igi

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	A	B	C	D	E	F	G
1							
2	File Format:		GIBBS		C:\HSC5\Gibbs\Rx134AGibbsIn.igi		
3	Pure Substances in the Last Phase		NO				
4	Increase Temperature	101	Steps		Criss-Cobble On		
5	Temperature Range:	200.000	2200.000	C			
6	Pressure Range:	1.000	1.000	bar			
7							
8	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
9	GASES						
10	Co(g)	25.000					1.000
11	O2(g)	25.000					1.000
12	SO2(g)	25.000					1.000
13	OXIDES, etc.		1.000	100.000			
14	CoO	25.000					1.000
15	Co3O4	25.000					1.000
16	CoSO4	25.000	1.000	100.000			1.000
17	ELEMENTS						
18	Co	25.000					1.000
19							
20							
21							

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Reaction 134B
CoO + SO2(g) + H2O(g) = CoSO4 + H2(g)

Fig. 2. Reaction 134B equilibrium picture.

Table 2. Reaction 132B equilibrium calculation input
Reaction 134B
CoO + SO2(g) + H2O(g) = CoSO4 + H2(g)

	A	B	C	D	E	F	G
		Equilibrium Calculations C:\HSC5\Gibbs\Rx134BGibbsIn.igi					
		File Edit View Insert Delete Format Units Calculate Help					
	A1						
1							
2	File Format:		GIBBS		C:\HSC5\Gibbs\Rx134BGibbsIn.igi		
3	Pure Substances in the Last Phase		NO				
4	Increase Temperature	101	Steps		Criss-Cobble On		
5	Temperature Range:	0.000	500.000	C			
6	Pressure Range:	1.000	1.000	bar			
7							
8	SPECIES Formula	Temper. C	Amount kmol	Amount %	Step kmol	Step %	Activity Coeff.
9	GASES		1.000	100.000			
10	H2(g)	25.000					1.000
11	H2O(g)	25.000					1.000
12	O2(g)	25.000					1.000
13	SO2(g)	25.000	1.000	100.000			1.000
14	OXIDES, etc.		2.000	100.000			
15	CoO	25.000	1.000	50.000			1.000
16	Co3O4	25.000					1.000
17	CoSO4	25.000					1.000
18	CoSO4*6H2O	25.000					1.000
19	CoSO4*7H2O	25.000					1.000
20	H2O	25.000	1.000	50.000			1.000
21	H2SO4	25.000					1.000
22	ELEMENTS						
23	Co	25.000					1.000
24							
25							

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Exit | Ins Phase | Del Phase | Ins Row | Del Row | **Open** | \HSC5\Gibbs\Rx134BGibbsIn.i | Save | Gibbs

The exotherm from reaction 134B together with the heat content in the reactants requires a 67.20 MJ cooler to maintain 105°C in the reactor.

The H2 product from reactor 134B is cooled to 25°C in H2 Cooler 134B, and scrubbed with 0.667 mole of the feed water before it is discharged.

A simplified flowsheet for this cycle is shown in Fig. 3.

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

[3] M. Ducarroir, H. Romero-Paredes, D. Steinmetzt, F. Sibieude and M. Tmar, On The Kinetics Of The Thermal Decomposition Of Sulfates Related with Hydrogen Water Splitting Cycles, Int. J. Hydrogen Energy, Vol. **9**. No. 7, pp. 579-585, 1984.

Scrubber 134A

○3.1

O₂/Air (g) Product

H₂O Feed

○1.2

○3

O₂/Air(g)

H₂O(l)

○1.3

Condenser 134A
Duty = -29.12 MJ
Pressure = 2.39 bar
Power = 1.72 kW
Heat eq. = 16.27 MJ

SO₂(l)

○5

H₂(g) Product

○2.2

Scrubber 134B

○1

H₂O Feed

H₂O

Gas Compressor 134A
4 kW = 37.9 MJ Heat eq.

○4.2

○4.1

SO₂(g) + O₂(g)

Offgas Cooler 134A
Total Duty = -152.06 MJ
-43.11 MJ Recovered in Dryer 134B

H₂ Cooler 134B
-5.03 MJ

H₂ + H₂O

○2.1

Cooler 134B
Duty = -67.20 MJ

○1.1

○4

○2

○7

CoSO₄ • H₂O(s)

REACTOR 134A

CoSO₄ = CoO + SO₂ + 0.5 O₂
dG = 0 at 1006°C

T = 1500°C

CoO

○6

REACTOR 134B

CoO + SO₂ + H₂O = CoSO₄ + H₂
dG = 0 at 190°C

T = 105°C

CoSO₄ • H₂O(s)

H₂O(g)

○7.3

H₂O(g

○6.1

H₂O(g)

○7.2

○7.1

CoSO₄ • H₂O(s)

Solar Heater 134A
Duty = 489.58 MJ

○7.4

CoSO₄(s)

Purge Air

○8.1

Air Preheater 134A, Duty = 48.23 MJ

Purge Air

○8

CoSO₄ Dryer 134B
Total Duty = 43.11 MJ
All heat recovered from Offgas Cooler 134A

○7.4

CoSO₄(s)

System Thermal Efficiency =   17.9%

Fig. 3. PID 134 flowsheet.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 147 – CADMIUM SULFATE

This process is based on the following chemical reactions from Ref. [1]:

Reaction No.	Formula	Max. Temp. (°C)
147A	CdSO4 = CdO + SO2 + 0.5 O2	1000
147B	CdO + SO2 + H2O = CdSO4 + H2	200

SUMMARY

Using the 0.740 mole H2 yield that was determined by the equilibrium calculations, the maximum thermal efficiency from the PID 147 cycle is predicted to be 55.0%. This is sufficiently high to justify a more rigorous evaluation, even though it may be difficult to condense and remove the Cd metal from Offgas Cooler 147A. This efficiency calculation assumes that the H2 product can be removed from the process before it enters side reactions that could form CdS, H2S, or S.

Experimental data would be useful to quantify the kinetics of the reactions and yields of the product species.

A simplified flowsheet for this cycle is shown in Fig. 1 below.

REACTION 147A

Calculations using Ref. [2] show that reaction 147A is spontaneous at temperatures above 1097°C, where delta G is zero. The 1000°C maximum temperature specified for this reaction is too low, and was increased to 1150°C. The 1150°C operating temperature can be maintained with a 320.83 MJ solar heater.

After receiving a comment that a part of the Cd is bound as (CdO)2*CdSO4 so that the required recycle will increase. The PID 147 cycle was recalculated using (CdO)2*CdSO4 as a reaction product from reaction 147A. With a 1150°C reactor temperature, the reaction products were calculated using the Equilibrium Module in Ref. 2 as follows: CdO = 0.348 mole, (CdO)2*CdSO4 = 0.209 mole, SO2 = 0.747 mole, O2 = 0.374 mole, SO3 = 0.0229 mole, and Cd gas = 0.0033 mole. Production of very small quantities of other species were also indicated by these calculations. The 1 mole air purge and 0.0211 mole of the CdSO4 remain unreacted.

The air purge sweeps the SO2/ O2 offgas mixture from Reactor 147A into the SO2 separation system. The purge air is preheated by CdO as it exits Reactor 147A. The Reactor 147A offgas mixture is cooled to 40°C in Offgas Cooler 147A. Ninety three percent of the heat from this cooler is recuperated in CdSO4 Heater 134B. The 7% excess heat in Offgas Cooler 147A is rejected.
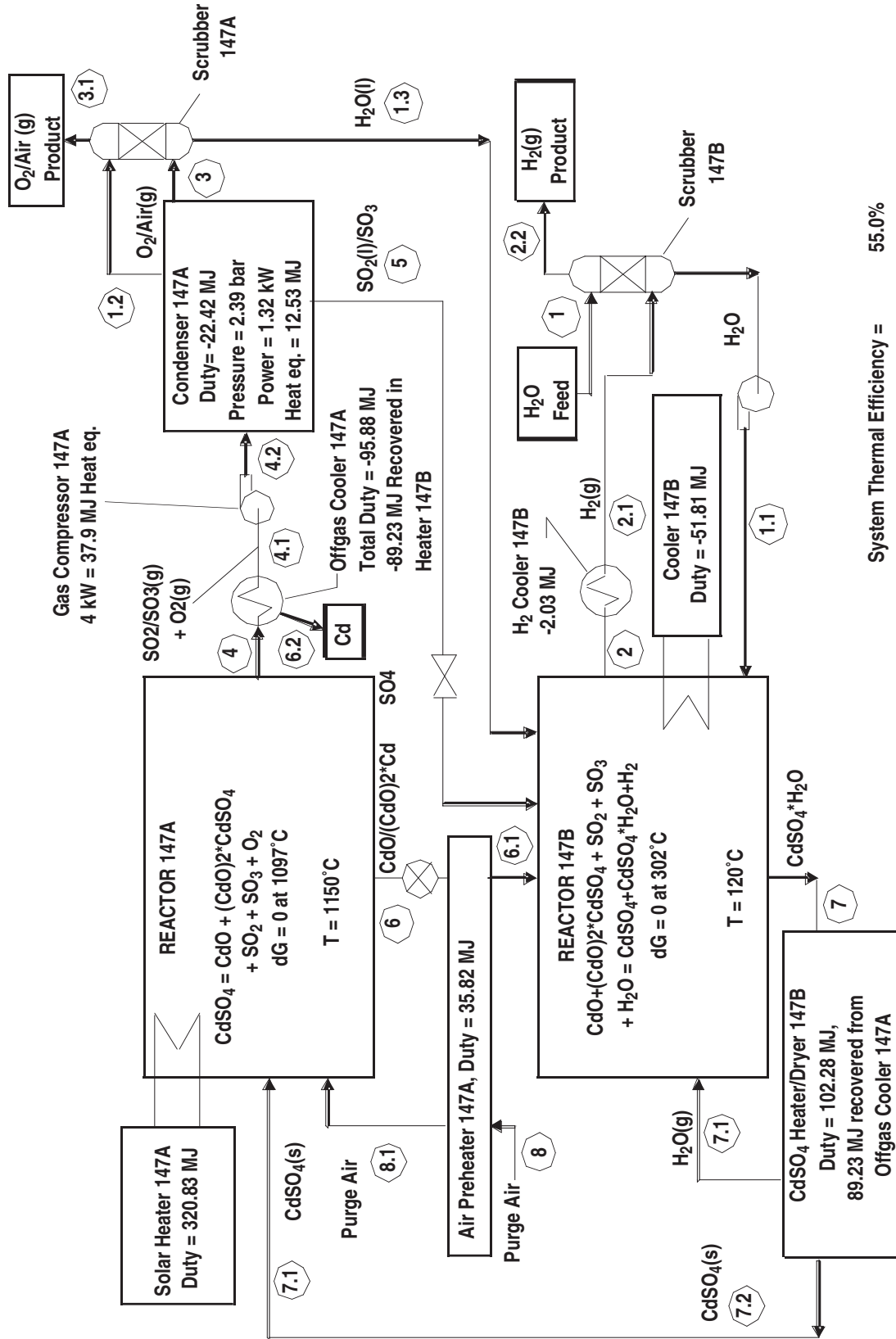
Fig. 1. PID 147 flowsheet.

Following cooling, the gases are compressed, and cooled in Condenser 147A to liquefy the SO2 and solidify the ~3% SO3. The O2 is scrubbed with 0.333 mole feed H2O and removed with the purge air as product. The liquid SO2 and solid SO3 are fed with the CdO and (CdO)2*CdSO4 from Reactor 147A and H2O from the scrubbers into Reactor 147B.

REACTION 147B

The equilibrium for reaction 147B lies to the right at temperatures below 302°C. The 200°C temperature specified for Reactor 147B is workable. A 120°C temperature was selected for this assessment, however, because it is adequate to vaporize the feed water and to remove the most of the waters of hydration before the CdSO4 is transferred to Heater 147B. Heater 147B recovers 89.23 MJ from Offgas Cooler 147A, and adds 13.05 MJ heat to increase the CdSO4 temperature to 888°C. The CdSO4 is then transferred into reactor 147A. The formation of sulfides was not included in the equilibrium calculations because the kinetics for their formation is slow.

The exotherm from reaction 147B together with the heat content in the reactants requires a 51.81 MJ cooler to maintain 120°C in the reactor.

The 0.740 mole H2 product from reactor 147B is cooled to 25°C in H2 Cooler 147B with a heat rejection of 2.03 MJ, and scrubbed with 0.656 mole of the feed water before it is discharged.

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows", Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 149 – BARIUM-MOLYBDENUM SULFATE

This cycle is based on the following chemical reactions from Ref. [1]:

Reaction No.	Formula	Max. Temp. (°C)
149A	BaSO4 + MoO3 = BaMoO4 + SO2 + 0.5 O2	1000
149B	BaMoO4 + SO2 + H2O = BaSO4 + MoO3 + H2	25

SUMMARY:

When the specified H2 output of 1 mole is assumed, a maximum thermal efficiency of the PID 149 cycle of 46.7% is predicted. When the H2 output is calculated with the equilibrium module of Ref. 2, however, the H2 yield decreases to 0.751 mole with a corresponding decrease in thermal efficiency to 28.0%. This is sufficiently low to preclude a more rigorous evaluation.

Discussions of each reaction along with a simplified flowsheet (Fig. 1) are shown below.

REACTION 149A

Calculations using Ref. 2 show that reaction 149A is spontaneous at temperatures above 944°C, where delta G is zero. The 1000°C maximum temperature specified in Ref. 1 for this reaction produces very small yields, and should be increased to at least 2000°C to achieve an O2 yield of 0.375 mole. A 2000°C operating temperature can be maintained with a 712.72 MJ solar heater.

An air purge sweeps the SO2/ O2 offgas mixture from Reactor 149A into the SO2 separation system. The purge air is preheated by the BaMoO4 as it is discharged from Reactor 149A. The Reactor 149A offgas mixture is cooled to 40°C in Offgas Cooler 149A. Forty four percent of the 209.68 MJ total heat from this cooler is recuperated in Heater 149B. The 56% excess heat from Offgas Cooler 149A is rejected.

Following cooling, the gases are compressed, and cooled in Condenser 149A to liquefy the SO2. The O2/air mixture is scrubbed with 0.333 mole feed H2O, and is removed together as product. The liquid SO2 is fed with the BaMoO4 from Reactor 149A and H2O from the scrubbers into Reactor 149B.

Although calculations using Ref. 2 indicate that the SO2 + O2 offgas mixture from Reactor 149A will react to form SO3 when cooled below 32°C, a catalyst is required to promote this reaction. Also, when the SO2 is condensed from a 40°C gas to a liquid, it exists as a cold gas for only a brief time duration.
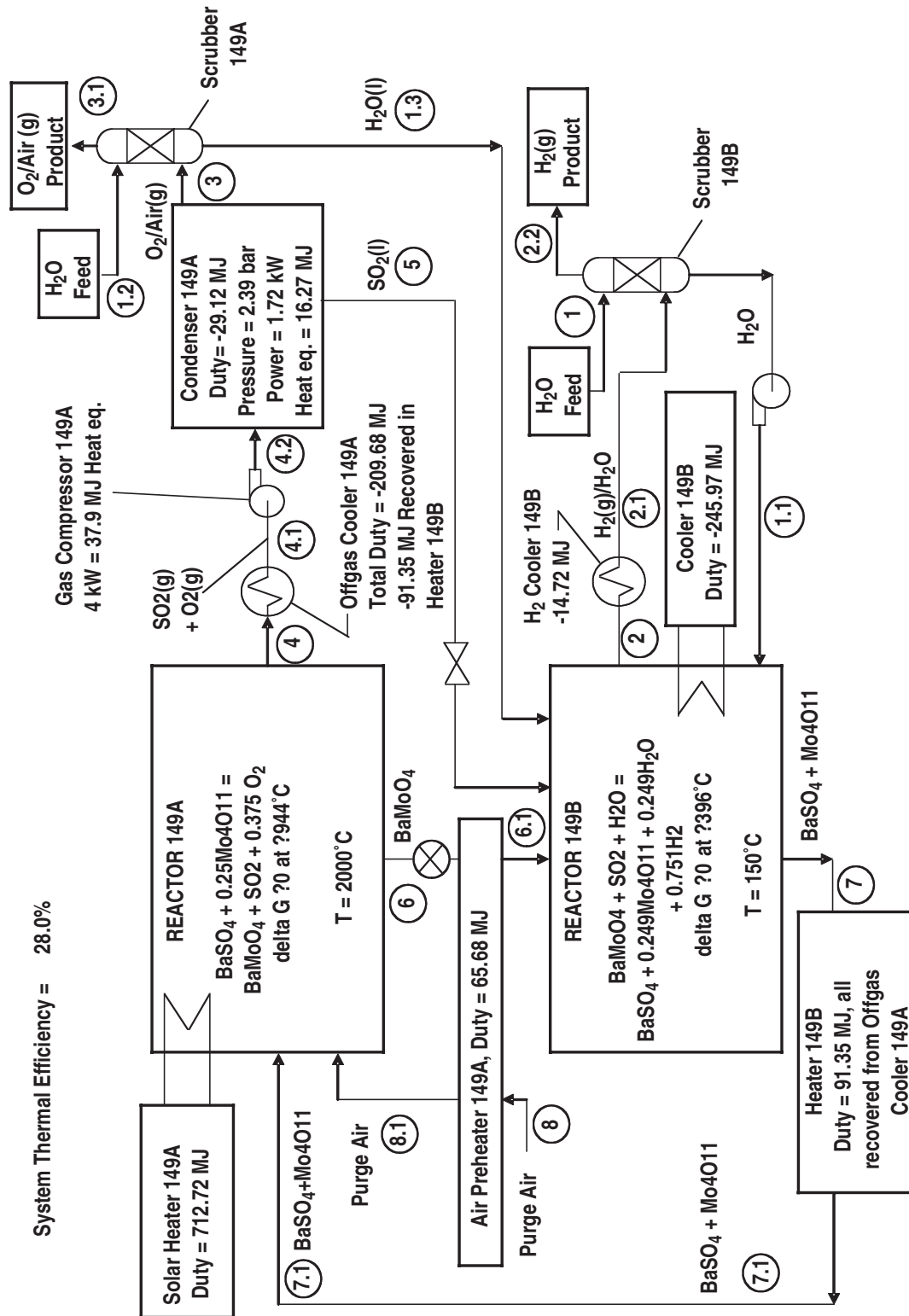
Fig. 1. Solar hydrogen generation project, PID 149 flowsheet, Rev. 2.

A2-138
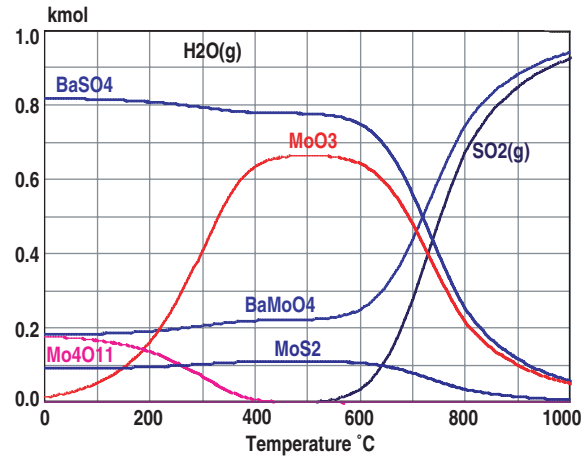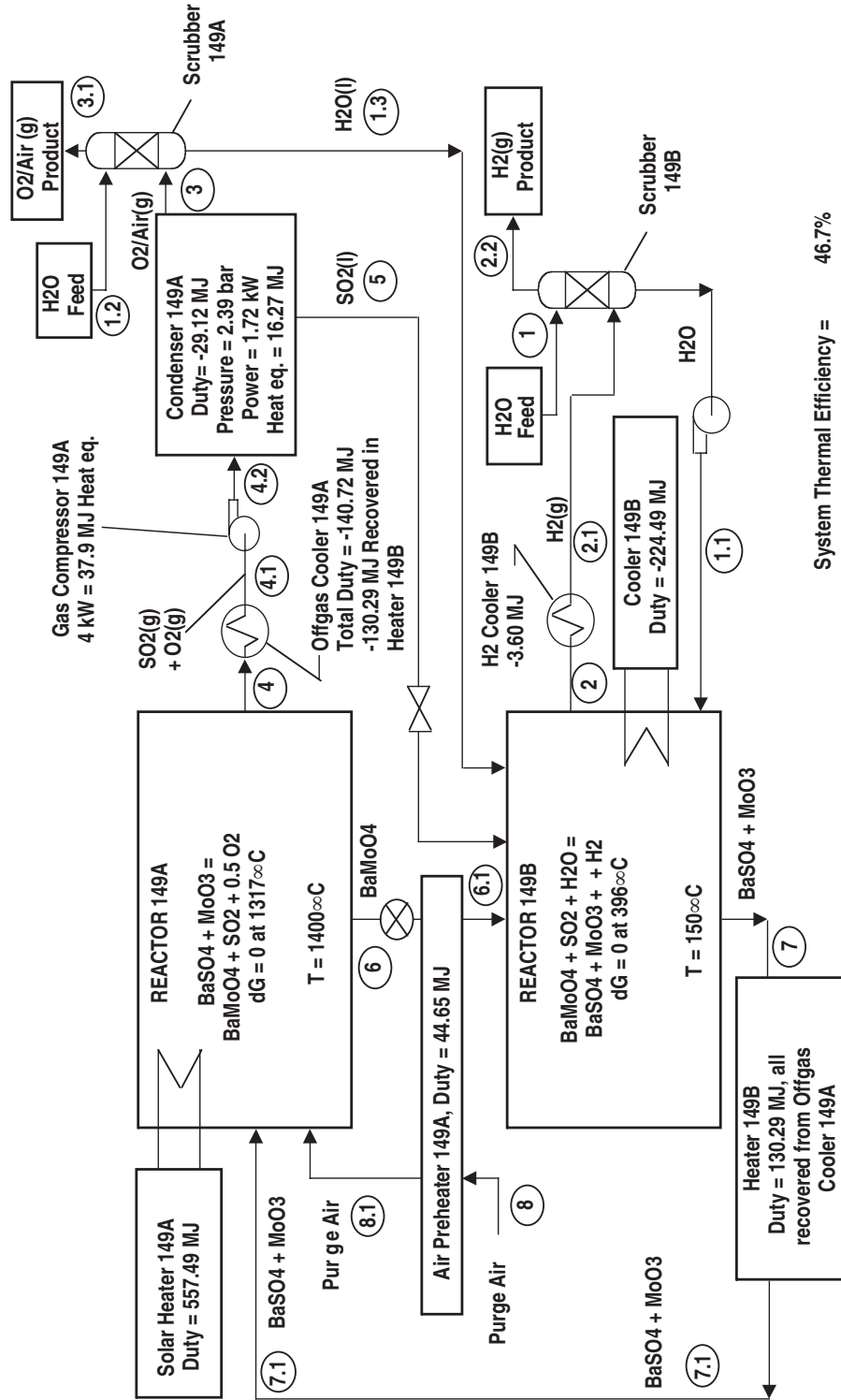
REACTION 149B

Reaction 149B is spontaneous at temperatures below 396°C, where delta G is zero.

Equilibrium calculations for this reaction indicate that the reaction produces Mo_4O_{11} instead of MoO_3, with 0.751 mole H_2 product.

The 25°C temperature specified for reaction 149B is workable. A 150°C temperature was selected for this assessment, however, because it will vaporize the feed water and facilitate separation of the $BaSO_4$ and Mo_4O_{11} solids from the gaseous components. The $BaSO_4$ and Mo_4O_{11} are transferred to Heater 149B. Heater 149B recovers 91.35 MJ from Offgas Cooler 149A to increase the $BaSO_4$ / Mo_4O_{11} mixture temperature to 700°C. These solids are then transferred to reactor 149A.

The exotherm from reaction 149B together with the heat content in the reactants requires a 245.97 MJ cooler to maintain 150°C in the reactor.

The 0.751 mole H_2 and 0.249 mole $H_2O(g)$ from reactor 149B are cooled to 25°C in H_2 Cooler 149B with a heat rejection of 14.72 MJ. The H_2 is scrubbed with 0.667 mole of the feed water before it is discharged as product.

It should be noted, that if reduced sulfur species (H_2S, S, and MoS_2) are allowed in the HSC calculation, then no H_2 is evolved and the efficiency is zero.

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows", Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 151 –CARBON-SULFUR

This cycle is based on the following chemical reactions from Ref. [1]:

Reaction No.	Formula	Max. Temp. (°C)
151A	$H_2SO_4(g) = SO_2(g) + H_2O(g) + 0.5\ O_2(g)$	950
151B	$CO_2(g) + SO_2(g) + H_2O(g) = CO(g) + H_2SO_4(l)$	350
151C	$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$	500

SUMMARY

Calculations for reaction 151B (Ref. [1] Reaction Code CO2-9) show delta G > 0 for all temperatures below 3000°C. **This indicates that PID 151 is not workable as presented in the UNLV database, and further evaluation of this cycle is unnecessary**.

REACTION 151A

Calculations using Ref. [2] show that reaction 151A is spontaneous at temperatures above 486°C, where delta G is zero (Table 1 below). The 950°C maximum temperature specified in Ref. 1 for this reaction is sufficient.

REACTION 151B

Reference [2] data for reaction 151B (Reaction Code CO2-9) show delta G > 0 for all temperatures below 3000°C (Table 2). This indicates that PID 151 is not workable as presented in the UNLV database, and further evaluation of this cycle is unnecessary.

REACTION 151C

The equilibrium for reaction 151C lies to the right at temperatures below 816°C (Table 3). The 500°C temperature specified for reaction 149B is workable, but could be reduced to achieve more favorable kinetics.

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

TABLE 1 - REACTION EQUATION 151A DATA (FROM REF. 2)
Note that Reaction 151A is spontaneous above 486°C (759 K) where delta G = 0

Reaction 151A
RX151A
H2SO4 = SO2(g) + H2O(g) + 0.5O2(g)
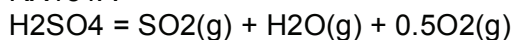
T	deltaH	deltaS	deltaG	K	Log(K)
C	Kcal	cal/K	kcal		
0	68.564	101.172	40.928	1.78E-33	-32.75
100	64.818	88.514	31.789	2.40E-19	-18.62
200	63.347	85.026	23.117	2.10E-11	-10.679
300	61.808	82.076	14.766	2.34E-06	-5.631
400	60.255	79.577	6.687	6.74E-03	-2.171
500	58.708	77.436	-1.161	2.13E+00	0.328
600	57.176	75.571	-8.809	1.60E+02	2.205
700	55.665	73.933	-16.283	4.54E+03	3.657
800	54.186	72.486	-23.602	6.41E+04	4.807
900	52.748	71.204	-30.786	5.44E+05	5.736
1000	51.351	70.061	-37.848	3.14E+06	6.498
1100	49.992	69.034	-44.802	1.35E+07	7.131
1200	48.672	68.105	-51.658	4.62E+07	7.664

Formula	FM	Conc.	Amount	Amount	Volume	
	g/mol	wt-%	mol	g	l or ml	
H2SO4	98.073	100	1	9.81E+01	53.272	ml
	g/mol	wt-%	mol	g	l or ml	
SO2(g)	64.059	65.317	1	6.41E+01	22.414	l
H2O(g)	18.015	18.369	1	1.80E+01	22.414	l
O2(g)	31.999	16.314	0.5	1.60E+01	11.207	l

Rx151A from 480 to 500C
H2SO4 = SO2(g) + H2O(g) + 0.5O2(g)
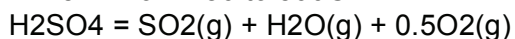
T	deltaH	deltaS	deltaG	K	Log(K)
C	kJ	J/K	kJ		
480	246.926	325.682	1.639	7.70E-01	-0.114
481	246.861	325.596	1.313	8.11E-01	-0.091
482	246.797	325.511	0.987	8.55E-01	-0.068
483	246.732	325.426	0.662	9.00E-01	-0.046
484	246.668	325.34	0.336	9.48E-01	-0.023
485	246.603	325.255	0.011	9.98E-01	-0.001
>486	246.539	325.17	-0.314	1.05E+00	0.022
487	246.474	325.085	-0.639	1.11E+00	0.044
488	246.41	325	-0.964	1.17E+00	0.066
489	246.345	324.915	-1.289	1.23E+00	0.088
490	246.281	324.831	-1.614	1.29E+00	0.11
491	246.216	324.746	-1.939	1.36E+00	0.133
492	246.152	324.662	-2.264	1.43E+00	0.155
493	246.087	324.578	-2.588	1.50E+00	0.176
494	246.023	324.494	-2.913	1.58E+00	0.198
495	245.958	324.41	-3.237	1.66E+00	0.22

496	245.894	324.326	-3.562	1.75E+00	0.242
497	245.829	324.242	-3.886	1.84E+00	0.264
498	245.765	324.158	-4.21	1.93E+00	0.285
499	245.7	324.075	-4.534	2.03E+00	0.307
500	245.636	323.991	-4.858	2.13E+00	0.328

Formula	FM g/mol	Conc. wt-%	Amount mol	Amount g	Volume l or ml	
H2SO4	98.073	100	1	9.81E+01	53.272	ml
	g/mol	wt-%	mol	g	l or ml	
SO2(g)	64.059	65.317	1	6.41E+01	22.414	l
H2O(g)	18.015	18.369	1	1.80E+01	22.414	l
O2(g)	31.999	16.314	0.5	1.60E+01	11.207	l

TABLE 2 - REACTION EQUATION 151B DATA (FROM REF. 2) –
Note that reaction 151B (Reaction Code CO2-9) is nonspontaneous from 0 to 3000°C

Reaction 151B (STCH Reaction Code CO2-9) from 0 to 3000°C
CO2(g) + SO2(g) + H2O(l) = CO(g) + H2SO4(ia)
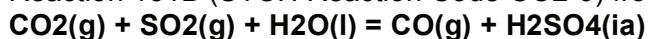
T	deltaH	deltaS	deltaG	K	Log(K)
C	kJ	J/K	kJ		
0	-36.508	-288.712	42.354	7.94E-09	-8.1
100	-68.172	-386.942	76.215	2.14E-11	-10.67
200	-106.727	-478.152	119.51	6.39E-14	-13.195
300	-152.837	-566.308	171.742	2.22E-16	-15.653
400	-207.948	-654.773	232.812	8.57E-19	-18.067
500	-269.576	-740.032	302.58	3.60E-21	-20.444
600	-337.367	-822.413	380.723	1.67E-23	-22.778
700	-411.263	-902.479	466.985	8.55E-26	-25.068
800	-491.232	-980.653	561.156	4.83E-28	-27.316
900	-577.242	-1057.24	663.063	2.98E-30	-29.525
1000	-669.272	-1132.49	772.56	2.00E-32	-31.699
1100	-767.305	-1206.59	889.523	1.44E-34	-33.84
1200	-871.331	-1279.69	1013.845	1.12E-36	-35.952
1300	-981.34	-1351.92	1145.432	9.21E-39	-38.036
1400	-1097.33	-1423.38	1284.203	8.03E-41	-40.095
1500	-1219.29	-1494.16	1430.086	7.38E-43	-42.132
1600	-1347.21	-1564.33	1583.015	7.12E-45	-44.148
1700	-1481.11	-1633.96	1742.934	7.18E-47	-46.144
1800	-1620.96	-1703.08	1909.79	7.54E-49	-48.123
1900	-1766.78	-1771.77	2083.536	8.23E-51	-50.085
2000	-1918.55	-1840.04	2264.129	9.30E-53	-52.032
2100	-2076.28	-1907.93	2451.53	1.09E-54	-53.964
2200	-2239.96	-1975.48	2645.704	1.31E-56	-55.884
2300	-2409.59	-2042.71	2846.616	1.62E-58	-57.791
2400	-2585.16	-2109.65	3054.236	2.06E-60	-59.686
2500	-2766.68	-2176.3	3268.536	2.69E-62	-61.571
2600	-2954.15	-2242.71	3489.488	3.59E-64	-63.445
2700	-3147.57	-2308.88	3717.07	4.90E-66	-65.31
2800	-3346.93	-2374.82	3951.256	6.83E-68	-67.165
2900	-3552.23	-2440.56	4192.027	9.72E-70	-69.013
3000	-3763.48	-2506.1	4439.361	1.41E-71	-70.852
H2O(l)		Extrapolated from		6.10E+02	K
H2SO4(ia)		Extrapolated from		3.98E+02	K

Formula	FM	Conc.	Amount	Amount	Volume	
	g/mol	wt-%	mol	g	l or ml	
CO2(g)	44.01	34.905	1	44.01	22.414	L
SO2(g)	64.059	50.807	1	64.059	22.414	L
H2O(l)	18.015	14.288	1	18.015	18.069	Ml
	g/mol	wt-%	mol	g	l or ml	
CO(g)	28.01	22.216	1	28.01	22.414	L
H2SO4(ia)	98.073	77.784	1	98.073	0	Ml

TABLE 3 - REACTION EQUATION 151C DATA (FROM REF. 2) –
Note that reaction 151C is spontaneous from 0 to 816°C (1089 K) where delta G = 0.

Reaction 151C (STCH Reaction Code CO-7), 0 to 1000°C
$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$
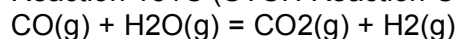
T	deltaH	deltaS	deltaG	K	Log(K)
C	Kcal	cal/K	kcal		
0	-9.848	-10.103	-7.088	4.70E+05	5.672
100	-9.747	-9.797	-6.091	3.70E+03	3.568
200	-9.58	-9.403	-5.131	2.35E+02	2.37
300	-9.374	-9.008	-4.211	4.03E+01	1.606
400	-9.142	-8.636	-3.329	1.21E+01	1.081
500	-8.896	-8.295	-2.483	5.03E+00	0.702
600	-8.646	-7.992	-1.668	2.62E+00	0.418
700	-8.398	-7.722	-0.883	1.58E+00	0.198
800	-8.154	-7.483	-0.123	1.06E+00	0.025
900	-7.919	-7.274	0.615	7.68E-01	-0.115
1000	-7.695	-7.091	1.333	5.91E-01	-0.229

Formula	FM	Conc.	Amount	Amount	Volume	
	g/mol	wt-%	mol	g	l or ml	
CO(g)	28.01	60.858	1	2.80E+01	22.414	l
H2O(g)	18.015	39.142	1	1.80E+01	22.414	l
	g/mol	wt-%	mol	g	l or ml	
CO2(g)	44.01	95.62	1	4.40E+01	22.414	l
H2(g)	2.016	4.38	1	2.02E+00	22.414	l

Reaction 151C (STCH Reaction Code CO-7), 800 to 820°C
$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$
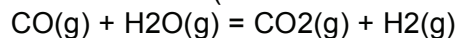
T	deltaH	deltaS	deltaG	K	Log(K)
C	Kcal	cal/K	kcal		
800	-8.154	-7.483	-0.123	1.06E+00	0.025
801	-8.151	-7.481	-0.116	1.06E+00	0.024
802	-8.149	-7.479	-0.108	1.05E+00	0.022
803	-8.147	-7.477	-0.101	1.05E+00	0.02
804	-8.144	-7.474	-0.093	1.04E+00	0.019
805	-8.142	-7.472	-0.086	1.04E+00	0.017
806	-8.139	-7.47	-0.078	1.04E+00	0.016
807	-8.137	-7.468	-0.071	1.03E+00	0.014
808	-8.135	-7.466	-0.063	1.03E+00	0.013
809	-8.132	-7.463	-0.056	1.03E+00	0.011
810	-8.13	-7.461	-0.048	1.02E+00	0.01
811	-8.127	-7.459	-0.041	1.02E+00	0.008
812	-8.125	-7.457	-0.033	1.02E+00	0.007
813	-8.123	-7.455	-0.026	1.01E+00	0.005
814	-8.12	-7.452	-0.018	1.01E+00	0.004
815	-8.118	-7.45	-0.011	1.01E+00	0.002
>816	-8.115	-7.448	-0.004	1.00E+00	0.001
817	-8.113	-7.446	0.004	9.98E-01	-0.001
818	-8.111	-7.444	0.011	9.95E-01	-0.002
819	-8.108	-7.441	0.019	9.91E-01	-0.004
820	-8.106	-7.439	0.026	9.88E-01	-0.005

Formula	FM g/mol	Conc. wt-%	Amount mol	Amount g	Volume l or ml	
CO(g)	28.01	60.858	1	2.80E+01	22.414	l
H2O(g)	18.015	39.142	1	1.80E+01	22.414	l
	g/mol	wt-%	mol	g	l or ml	
CO2(g)	44.01	95.62	1	4.40E+01	22.414	l
H2(g)	2.016	4.38	1	2.02E+00	22.414	l

PID 152 – IRON-ZINC

This process is based on the following proposed chemical reactions from the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Fe3O4-9	2Fe3O4(s) + 3Zn(l) + 4H2O(g) = 3ZnFe2O4(s) + 4H2(g)	1	600
ZnFe2O4	3ZnFe2O4(s) = 2Fe3O4(s) + 3Zn(g) +2O2(g)	1	1300

SUMMARY

The proposed cycle does not operate at the proposed temperature for reaction ZnFe2O4, but must operate at over 2000°C, where the efficiency of the cycle is less than 23.5%.
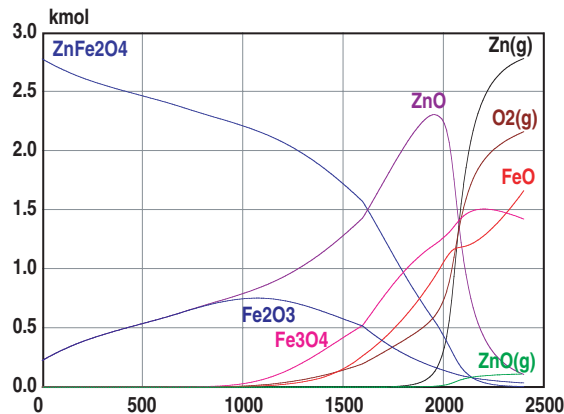
DISCUSSION

The reactions are unique to the proposed cycle.

HSC-5 data shows that delta G = 0 at 1400 C for the Fe3O4-9 reaction, and the reactor can work at the proposed temperature, where delta G = -84 kJ.

ZnFe2O4 melts at 1590 C and substituting 3ZnFe2O4(l) results in delta G = 0 at 1996°C. At 1300 C, the equilibrium O2 vapor pressure would be less than 1.8×10^{-4} atm. At this small a partial pressure, a sweep gas must be used to drive the reaction, incurring a significant separation penalty. At 1300°C, more Fe2O3 than Fe3O4 is formed, further decreasing the mass efficiency. Therefore, the proposed reactor must operate above 2000°C.

If the ZnFe2O4 can be maintained at 600°C for feed to the ZnFe2O4 reactor and that reactor is operated at over 2000°C, The solar duty would be 2443 MJ for two moles of H2, resulting in an efficiency of 23.5%.

Therefore the proposed cycle does not operate at the proposed temperature 1300°C for reaction ZnFe2O4, but must operate at over 2000°C, where the efficiency of the cycle is less than 23.5%.

PID 153 – SODIUM-MANGANESE FERRITE-2

This process is based on the following chemical reactions:

Reaction Code	Formula	Multiplier	Temp (ºC)
CO2-10	$CO_2(g) + 2NaFeO_2(s) = Fe_2O_3(s) + Na_2CO_3(s)$	3	600
Fe2O3-7	$6Fe_2O_3(s) + 4Na_3MnFe_2O_6(s) = 4MnFe_2O_4(s) + 12NaFeO_2(s) + O_2(g)$	0.5	1000
MnFe2O4	$2MnFe_2O_4(s) + 3Na_2CO_3(s) + H_2O(g) = 2Na_3MnFe_2O_6(s) + 3CO_2(g) + H_2(g)$	1	800

These reactions are very similar to those given in PID 111. A change to the PID 111 process is made through the addition of Fe2O3 to the system. Reacting the Na-Mn-Fe-O compound with Fe2O3 has been shown to increase the yield of the oxygen producing step (2).

ANALYSIS

Empirical results for the individual reactions can be found in a number of sources [1–3]. Unfortunately, none of these sources shows that the process can function cyclically. An equilibrium analysis was performed using HSC-5 to determine the steady state composition of the products of each of the three steps making up this process. The analysis was iterative, with the products of one step being input to the next. The results, which are given in detail in the following sections, indicate that this process will not function cyclically. It is important to keep in mind that the analysis results from HSC-5 may be deficient in some ways, given the complexity of the system being analyzed. In particular, information related to the phase of the Na-Mn-Fe-O compound has been shown to be important [3] and may not be adequately described in the HSC-5 database.

REACTION CO2-10

The equilibrium composition of the products of the reaction of sodium ferrite and carbon dioxide is shown in Fig. 1. This is the composition at the first iteration of the equilibrium analysis. The results at the final iteration are shown in Fig. 2.

Comparing the two figures, it is evident that at steady state the sodium ferrite is no longer being decomposed to form hematite and sodium carbonate. This is a result of very limited carbon dioxide production in the hydrogen producing step of the process.
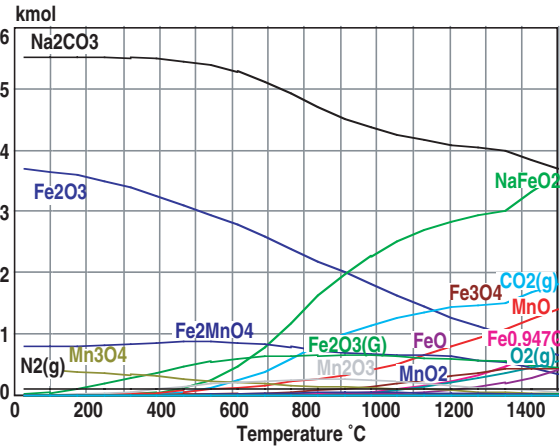
Fig. 1. Sodium ferrite decomposition, iteration 1.
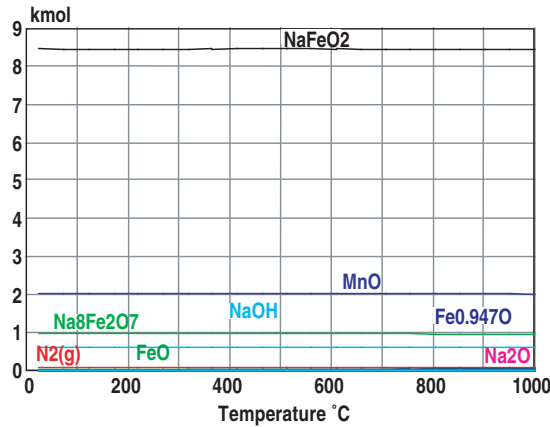
Fig. 2. Sodium ferrite decomposition, final iteration.

REACTION FE2O3-7

Figure 3 shows the equilibrium composition of the products formed by the reaction of the Na-Mn-Fe-O compound with hematite. This is the oxygen releasing step and the results shown in Fig. 3 are at an oxygen partial pressure of 1E-7 atm.

The reaction produces oxygen above 1000°C. However, very little MnFeO4 is produced, which is needed in the hydrogen producing step of the process. If the partial pressure of oxygen is not kept low (1E-7 atm), oxygen production drops significantly.

REACTION MNFE2O4

The product composition of the hydrogen generation reaction is shown in Fig. 4. The results indicate that very little hydrogen is produced (1.0E-2 kmol versus 1 kmol, the stoichiometric amount) and even then only at low hydrogen partial pressure (1e-5 atm).

Empirical results show that hydrogen is produced in amounts larger than those indicated by the equilibrium analysis [1]. The discrepancy likely results from the fact that very little magnesium ferrite was input to the reaction.
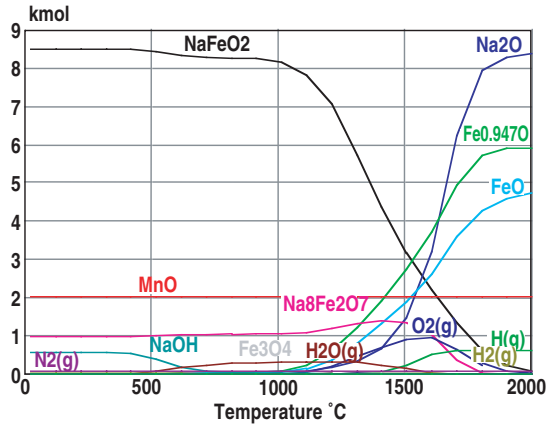
Fig. 3. Na-Mn-Fe-O decomposition, final iteration.
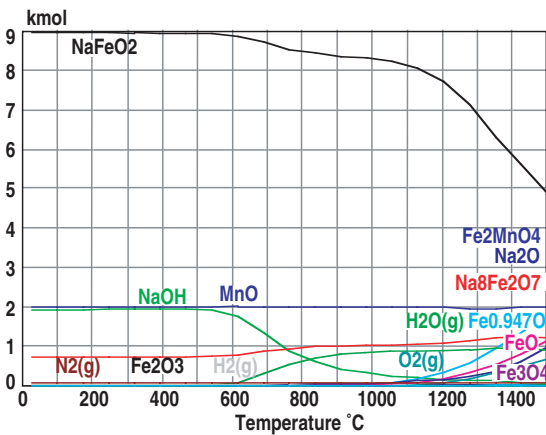
Fig. 4. Hydrogen production, final iteration.

CONCLUSIONS

The process appears to have several drawbacks that limit its viability as a practical means of producing hydrogen, they are:

1. Oxygen and hydrogen are produced only at very low pressures (1E-7 atm). Running a practical system at this pressure adds complexity and places restrictions on the types of receivers that can be used.

2. The ratio of hydrogen produced to ferrite oxidized is 0.5. This lowers overall system efficiency in that it requires more material to be processed for a given hydrogen yield. As a counterexample, the Fe3O4 / FeO system produces 1 mol of hydrogen for every mole of ferrite reduced, which is much more efficient.

3. Experimental results have not demonstrated that the process is cyclical. The equilibrium analysis indicates that it isn't, but this should be verified empirically.

This cycle is, therefore, determined to not be viable and has an efficiency of 0%.

REFERENCES

[1]   Tamaura, Y., Ueda, Y., Matsunami, J., Hasegawa, N., Nezuka, M., Sano, T., "Solar Hydrogen Production While Using Ferrites," *Solar Energy,* Vol. **65**, No. 1, pp. 55-57. 1999.

[2]   Kaneko, H., Hosokawa, Y., Gokon, N., Kojima, N., Hasegawa, N., Kitamura, M., Tamaura, Y., "Enhancement of O2-releasing step with Fe2O3 in the water splitting by MnFe2O4-Na2CO3 system," *J. Phys. Chem. Solids,* Vol. **62**, No. 7, pp. 1341-1347.

[3]   Kaneko, H., Ochiai, K., Gokon, N., Shimizu, Y., Hosokawa, N., Tamaura, Y., "Thermodynamic study based on the phase diagram of the Na2O-MnO-Fe2O3 system for H2 production in three-step water splitting with NaCO3/MnFe2O4/Fe2O3," *Solar Energy,* Vol. **72**, No. 4, pp. 377-383.

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PID 154 – SODIUM FERRITE

This process is based on the following proposed chemical reactions from the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (^{o}C)
CO2-11	CO2 + 2Na2FeO2 + H2O = Na2CO3 + 2NaFeO2 + H2	1	800
Na2CO3	2Na2CO3 + 4NaFeO2 = 2CO2 + 4Na2FeO2 + O2	0.5	2000

SUMMARY

The proposed 2-step cycle was proposed at 800°C for both steps, which is not feasible. We lack thermodynamic information on Na_2FeO_2. On the website, we have made an approximation (replacing Na_2FeO_2 with Na_2O + FeO) that perhaps the cycle could work between the temperatures of 800°C for the H_2 evolution step, and 2000°C for the O_2 evolution step. Until we have the thermodynamic data, we decided to not assess the cycle for efficiency, and assigned an efficiency of 0.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 160 – ARSENIC-IODINE

This process is based on the following chemical reactions in the UNLV database, for which no references are cited: The cycle is formally similar to PID 1, the Sulfur-Iodine cycle. One need only substitute the lower valence SO_2 with the lower valence As_2O_3, the higher valence SO_3 with As_2O_5, H_2SO_4 with H_3AsO_4, etc.

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
As2O3-2	$As_2O_3 + 2I_2(l) + 5H_2O(l) = 2H_3AsO_4(a) + 4HI(g)$	0.5	40 (electrochemical)
As2O5	$As_2O_5(s) = As_2O_3(g) + O_2(g)$	0.5	1500
H3AsO4	$2H_3AsO_4(s) = As_2O_5(s) + 3H_2O(g)$	0.5	250
HI-1	$2HI(g) = I_2(g) + H_2(g)$	1	300

AS2O3-2 REACTOR

The As2O3-2 reaction is unique to this cycle. HSC-5 data show delta G is negative above 896°C, but includes only H3AsO4(a) data. The positive delta G near room temperature tells us this cycle needs to be a hybrid. Equilib-Web data do not show any H3AsO4 produced at any temperature or pressure. HSC-5 equilibrium data show about 0.2 moles of As2O3, 0.3 moles of H3AsO3, and about 0.1 moles of H3AsO4 at 25°C, while about 0.9 moles of I2 remain unreacted, with AsI3 as the iodine product. No formation of HI is predicted below 200°C. Since As2O3 is only slightly soluble in water, an electrochemical reactor would require an alkali carbonate or hydrochloric acid solution. It is difficult to see how an electrochemical reactor could minimize the formation of unwanted products such as H3AsO3, AsI3, and As2O4. If all of these problems can be solved, the electrical energy requirement at 40°C in the reactor would be 352 MJ/kg-mole of H2 produced and 703 MJ at a source operating at 50% efficiency.

AS2O5 REACTOR

This reaction is also proposed for two other cycles. HSC-5 data show delta G is negative above 1144°C. HSC-5 equilibrium data show significant quantities of As2O4 below about 1400°C, which interferes with O2(g) production. Optimum conditions are about 2 bar and 1500°C, though small quantities of AsO, and AsO2 remain. If these contaminants are not a significant, the solar heat requirement for this reactor would be about 264 MJ/kg-mole of H2 produced.

H3ASO4 REACTOR

If the problems associated with the As2O3-2 reactor can be solved for adequate production of arsenic acid, HSC-5 data show that delta G is negative above 227°C.

HSC-5 equilibrium data show that decomposition by this reaction is possible above about 250°C without unwanted byproducts.

HI-1 SYSTEM

This reaction is also proposed at 300°C in many other PIDs, including PIDs 1, 82 and 160, which were selected for assessment. HSC-5 data shows delta G is slightly positive for all temperatures for this reaction, while K is slightly higher at higher temperatures. Fifty bar operating pressure is required to deliver pressurized hydrogen, and HSC-5 equilibrium data at 50 bar show about 0.17 moles of $H_2(g)$ and $I_2(g)$ generated at 300°C per mole of HI(g), with no change at lower pressures. This requires separation and recycle of unreacted HI within a system that contains a distillation column operating at 20 bar, as shown in Fig. 2 of Ref. [1]. The solar energy requirement for this system is 177 MJ per kg-mole of H_2 produced.

Since the As2O3-2 and As2O5 reactions produce unwanted byproducts that are not easily separated for recycle, this cycle is not technically feasible as proposed. If these problems could be overcome, a hybrid cycle efficiency of less than 25.0% is assured. Therefore, this cycle does not warrant further investigation.

REFERENCES

[1]   Engels, H., Knoche, K., Roth, M., "Direct Dissociation of Hydrogen Iodide – an Alternative to the General Atomic Proposal," *Int. J. Hydrogen Energy,* Vol. **12**, No. 10, pp. 675-678. 1987.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 162 – URANIUM CARBONATE-2

This process is based on the following chemical reactions from Ref. 1:

Reaction No.	Formula	Max. Temp. (°C)
162A	$3UO_3(s) = U_3O_8(s) + 0.5\ O_2(g)$	600
162B	$4\ CO_2 + U_3O_8(s) = CO + 3UO_2CO_3$	150
162C	$0.75\ UO_2CO_3 = 0.75CO_2(g) + 0.75\ UO_3$	600
162D	$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$	300

SUMMARY

The delta G for reaction 162B is >0 for all temperatures below 3000°C. **This indicates that PID 162 is not workable as presented in the UNLV database, and further evaluation of this cycle is unnecessary.**

REACTION 162A

Calculations using Ref. [2] show that reaction 177A is spontaneous at temperatures above 672°C, where delta G is zero (Table 1 and Fig. 1). The 600°C maximum temperature specified in Ref. [1] for this reaction is insufficient, and should be increased to at least 900°C.

REACTION 162B

Reference [2] data for reaction 162B (Reaction Code Co2-13 in Ref. [1]) show delta G > 0 for all temperatures below 3000°C (Table 2). **This indicates that PID 162 is not workable as presented in the UNLV database, and further evaluation of this cycle is unnecessary.**

REACTIONS 162C AND 162D

Because reaction 162B does not work, these reactions were not assessed.

REFERENCES

[1] UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2] Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.11 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

TABLE 1. DELTA G CALCULATIONS FOR REACTION 162A (REF. 2)

Reaction 162A is spontaneous at temperatures
above 672°C (945 K) where delta G = 0

Reaction 162A
$3UO_3(s) = U_3O_8(s) + 0.5 O_2(g)$
$3UO_3 = U_3O_8 + 0.5 O_2(g)$
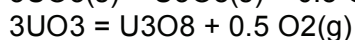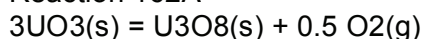
T	deltaH	deltaS	deltaG	K	Log(K)
C	kJ	J/K	kJ		
0	96.38	96.022	70.151	3.84E-14	-13.416
100	97.252	98.745	60.406	3.50E-09	-8.456
200	98.266	101.141	50.411	2.72E-06	-5.566
300	99.792	104.059	40.151	2.19E-04	-3.66
400	101.23	106.368	29.629	5.02E-03	-2.299
500	102.78	108.513	18.883	5.30E-02	-1.276
600	104.655	110.791	7.918	3.36E-01	-0.474
700	106.12	112.381	-3.243	1.49E+00	0.174
800	107.375	113.611	-14.546	5.11E+00	0.708
900	108.309	114.445	-25.952	1.43E+01	1.156
1000	108.805	114.854	-37.421	3.43E+01	1.535

Formula	FM	Conc.	Amount	Amount	Volume	
	g/mol	wt-%	mol	g	l or ml	
UO3	286.027	100	3	858.082	117.707	ml
	g/mol	wt-%	mol	g	l or ml	
U3O8	842.082	98.135	1	842.082	100.487	ml
O2(g)	31.999	1.865	0.5	15.999	11.207	l

$3UO_3 = U_3O_8 + 0.5 O_2(g)$
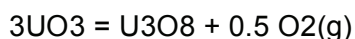
	T	deltaH	deltaS	deltaG	K	Log(K)
	C	kJ	J/K	kJ		
	670	105.697	111.94	0.122	9.85E-01	-0.007
	671	105.712	111.955	0.01	9.99E-01	-0.001
>	672	105.726	111.97	-0.102	1.01E+00	0.006
	673	105.74	111.985	-0.214	1.03E+00	0.012
	674	105.755	112	-0.326	1.04E+00	0.018
	675	105.769	112.015	-0.438	1.06E+00	0.024
	676	105.783	112.03	-0.55	1.07E+00	0.03
	677	105.797	112.045	-0.662	1.09E+00	0.036
	678	105.812	112.06	-0.774	1.10E+00	0.043
	679	105.826	112.075	-0.886	1.12E+00	0.049

680	105.84	112.09	-0.999	1.13E+00	0.055
681	105.854	112.105	-1.111	1.15E+00	0.061
682	105.868	112.12	-1.223	1.17E+00	0.067
683	105.883	112.135	-1.335	1.18E+00	0.073
684	105.897	112.149	-1.447	1.20E+00	0.079
685	105.911	112.164	-1.559	1.22E+00	0.085
686	105.925	112.179	-1.671	1.23E+00	0.091
687	105.939	112.193	-1.784	1.25E+00	0.097
688	105.953	112.208	-1.896	1.27E+00	0.103
689	105.967	112.223	-2.008	1.29E+00	0.109
690	105.981	112.237	-2.12	1.30E+00	0.115

Formula	FM g/mol	Conc. wt-%	Amount mol	Amount g	Volume l or ml	
UO3	286.027	100	3	8.58E+02	117.707	ml
	g/mol	wt-%	mol	g	l or ml	
U3O8	842.082	98.135	1	8.42E+02	100.487	ml
O2(g)	31.999	1.865	0.5	1.60E+01	11.207	l
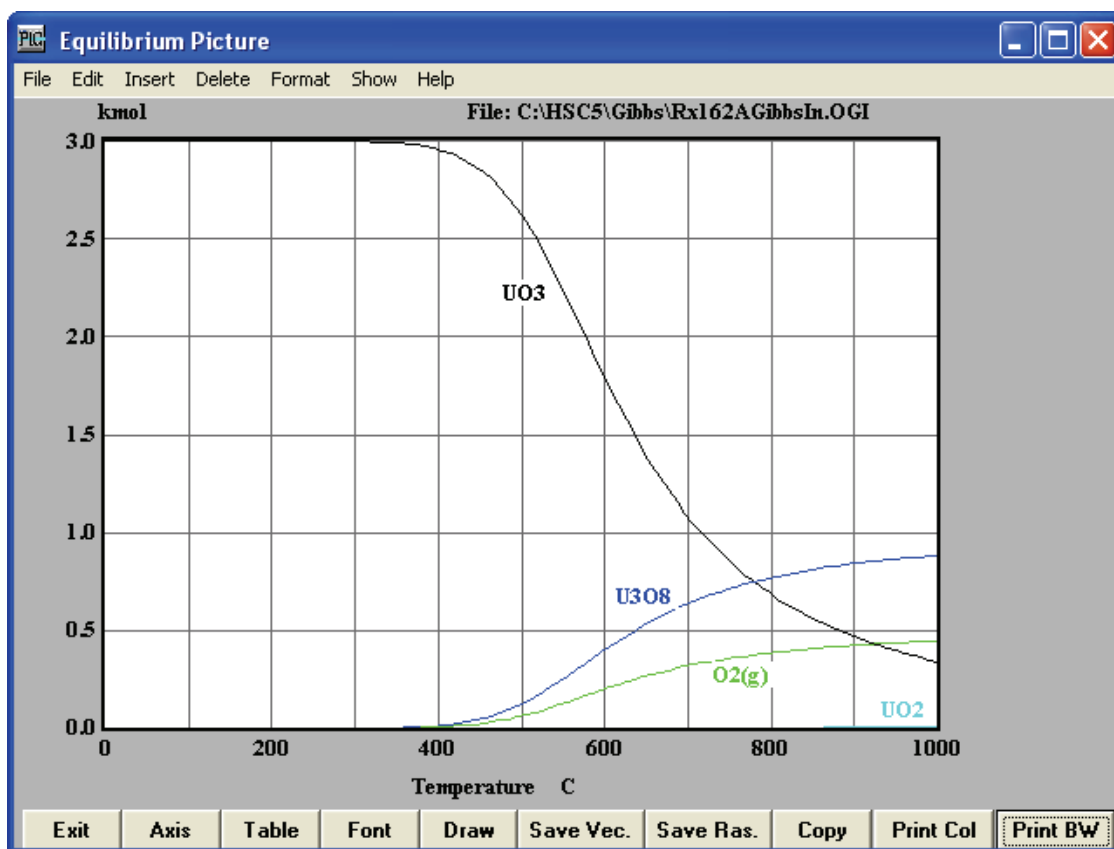
Fig. 1. Reaction 162A equilibrium picture.

TABLE 2. DELTA G CALCULATIONS FOR REACTION 162B (REF. 2)

Reaction 162B is nonspontaneous from 0 to 3000°C
Reaction 162B Temp = 150°C (per Ref. 1)

4 CO2 + U3O8(s) = CO + 3UO2CO3
4 CO2(g) + U3O8 = CO(g) + 3UO2CO3
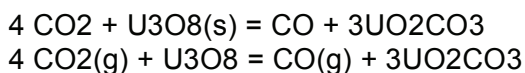
T	deltaH	deltaS	deltaG	K	Log(K)
C	kJ	J/K	kJ		
0	-36.123	-528.063	108.117	2.10E-21	-20.677
100	-34.62	-523.124	160.584	3.31E-23	-22.481
200	-35.086	-524.177	212.928	3.10E-24	-23.509
300	-36.519	-526.913	265.481	6.35E-25	-24.197
400	-37.756	-528.905	318.276	2.00E-25	-24.699
500	-38.729	-530.259	371.241	8.25E-26	-25.083
600	-39.508	-531.21	424.318	4.11E-26	-25.386
700	-39.297	-530.988	477.434	2.35E-26	-25.629
800	-38.294	-530.014	530.491	1.50E-26	-25.823
900	-36.382	-528.317	583.413	1.05E-26	-25.979
1000	-33.477	-525.946	636.131	7.92E-27	-26.101
1100	-29.517	-522.957	688.581	6.37E-27	-26.196
1200	-24.458	-519.406	740.704	5.42E-27	-26.266
1300	-18.265	-515.342	792.446	4.85E-27	-26.314
1400	-10.91	-510.813	843.757	4.53E-27	-26.344
1500	-2.371	-505.86	894.594	4.41E-27	-26.356
1600	7.371	-500.518	944.916	4.45E-27	-26.352
1700	18.331	-494.821	994.686	4.63E-27	-26.334
1800	30.523	-488.796	1043.869	4.97E-27	-26.303
1900	43.958	-482.469	1092.435	5.49E-27	-26.26
2000	58.649	-475.862	1140.354	6.22E-27	-26.206
2100	74.606	-468.994	1187.599	7.21E-27	-26.142
2200	91.841	-461.882	1234.144	8.55E-27	-26.068
2300	110.361	-454.543	1279.967	1.03E-26	-25.985
2400	130.176	-446.989	1325.046	1.28E-26	-25.894
2500	151.289	-439.237	1369.359	1.60E-26	-25.795
2600	173.692	-431.302	1412.887	2.05E-26	-25.689
2700	197.391	-423.195	1455.613	2.66E-26	-25.575
2800	222.393	-414.925	1497.521	3.50E-26	-25.456
2900	248.704	-406.501	1538.593	4.68E-26	-25.33
3000	276.327	-397.931	1578.816	6.34E-26	-25.198

U3O8		Extrapolated from		2000	K
UO2CO3		Extrapolated from		409	K

Formula	FM	Conc.	Amount	Amount	Volume	
	g/mol	wt-%	mol	g	l or ml	
CO2(g)	44.01	17.291	4	176.039	89.654	l
U3O8	842.082	82.709	1	842.082	100.487	ml
	g/mol	wt-%	mol	g	l or ml	
CO(g)	28.01	2.751	1	2.80E+01	22.414	l
UO2CO3	330.037	97.249	3	9.90E+02	0	ml

PID 163 – MANGANESE CARBONATE

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
CO2-14	$6CO_2 + 2Mn_3O_4(s) = 6MnCO_3 + O_2(g)$	0.5	100
CO-3	$CO(g) + H_2O(g) = CO_2(g) + H_2(g)$	1	300
MnCO3	$3MnCO_3 = CO + CO_2 + Mn_3O_4(s)$	1	600

SUMMARY

Because the CO2-14 and MnCO3 reactions are not technically feasible, this cycle is not technically feasible. No efficiency can be calculated based on the CO2-14 reaction, for which there is no temperature at which delta G = 0 and an electrochemical reaction is not feasible.

DISCUSSION

There are no references listed for this cycle and none were found in a search of the International Journal of Hydrogen Energy or Internet search.

CO2-14 REACTOR

The CO2-14 reaction is unique to this cycle. HSC-5 data for the CO2-14 reaction show delta G does not approach zero at any temperature. HSC-5 equilibrium data show a small amount of oxygen is generated above 1100°C; however, MnO is the dominant form above that temperature. Since all forms of Mn oxides are insoluble, an electrochemical step will also not work, therefore this reaction is not technically feasible.

CO-3 REACTOR

The CO-3 reaction is the classic water-gas shift reaction, proposed in PIDs 15, 46, 90, **91, 162 and 163**, the last three if which were selected for assessment. HSC-5 data show delta G is negative below 817°C with slow kinetics that are enhanced by catalysts in commercial practice. HSC-5 equilibrium data show a maximum in hydrogen production at 50 bar at about 1000°C and nearly zero at the proposed reactor temperature. In addition, unreacted steam, CO and CO2 must be separated for recycle and discharge of pressurized hydrogen. Therefore, this reaction will not work at the proposed temperature.

MnCO3 REACTOR

The MnCO3 reaction is unique to this cycle. HSC-5 data for the MnCO3 reaction show delta G < 0 above 495°C, with adequate kinetics at the proposed 600°C. However, HSC-5 equilibrium

data show no significant CO production below 1500°C, Mn3O4 nearly zero, and MnO as the dominant form at that temperature. Therefore, this reaction will not work as proposed.

Since the CO2-14 and MnCO3 reactions are not technically feasible, this cycle is not technically feasible. No efficiency can be calculated based on the CO2-14 reaction, for which there is no temperature at which delta G = 0 and an electrochemical reaction is not feasible.

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PID 177 – LEAD CARBONATE

This process is based on the following chemical reactions from Ref. [1]:

Reaction No.	Formula	Max. Temp. (°C)
177A	Pb3O4 = 3PbO + 0.5 O2	600
177B	6HCl + 3PbO = 3PbCl2(s) + 3H2O	400
177C	3PbCl2(s) + 4H2O = 6HCl + Pb3O4 + H2	500

CONCLUSIONS

Because the delta G for reaction 177C is >0 for all temperatures below 3000°C, and no H2 is produced, PID 177 is not workable as presented in the UNLV database, and further evaluation of this cycle is unnecessary.

REACTION 177A

Calculations using Ref. [2] show that reaction 177A is spontaneous at temperatures above 417°C, where delta G is zero. The 600°C maximum temperature specified in Ref. [1] for this reaction is sufficient, but should be increased to at least 1000°C to achieve more favorable kinetics and O2 yield (Table 1 and Fig. 1).

REACTION 177B

The equilibrium for reaction 177B lies to the right at temperatures below 1893°C. The 400°C temperature specified for this reaction is adequate (Table 2, Fig. 2).

REACTION 177C

Reference [2] data for reaction 177C (Reaction Code PbCl2) show delta G >0 for all temperatures below 3000°C, and no H2 is produced (Table 3 and Fig. 3). This indicates that PID 177 is not workable as presented in the UNLV database, and further evaluation of this cycle is unnecessary.

REFERENCES

[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

TABLE 1. REACTION 177A DELTA G CALCULATIONS (FROM REF. 2)

Reaction 177A is spontaneous above 417°C (690 K) where delta G = 0
From CRC Handbook: Pb3O4 decomposes at 500°C; m.p. PbO = 888°C
Reaction 177A Temp = 600°C (per Ref. 1)
Pb3O4 = 3PbO + 0.5 O2
Pb3O4 = 3PbO + 0.5O2(g)

	T	deltaH	deltaS	deltaG	K	Log(K)
	C	kJ	J/K	kJ		
	410	58.868	85.411	0.519	9.13E-01	-0.04
	411	58.85	85.385	0.434	9.27E-01	-0.033
	412	58.833	85.359	0.349	9.41E-01	-0.027
	413	58.815	85.333	0.263	9.55E-01	-0.02
	414	58.797	85.308	0.178	9.69E-01	-0.014
	415	58.779	85.282	0.093	9.84E-01	-0.007
	416	58.762	85.256	0.007	9.99E-01	-0.001
>	417	58.744	85.23	-0.078	1.01E+00	0.006
	418	58.726	85.205	-0.163	1.03E+00	0.012
	419	58.708	85.179	-0.248	1.04E+00	0.019
	420	58.691	85.153	-0.333	1.06E+00	0.025
	421	58.673	85.128	-0.418	1.08E+00	0.031
	422	58.655	85.102	-0.504	1.09E+00	0.038
	423	58.638	85.077	-0.589	1.11E+00	0.044
	424	58.62	85.052	-0.674	1.12E+00	0.05
	425	58.602	85.026	-0.759	1.14E+00	0.057
	426	58.585	85.001	-0.844	1.16E+00	0.063
	427	58.567	84.976	-0.929	1.17E+00	0.069
	428	58.549	84.95	-1.014	1.19E+00	0.076
	429	58.532	84.925	-1.099	1.21E+00	0.082
	430	58.514	84.9	-1.184	1.22E+00	0.088

Formula	FM	Conc.	Amount	Amount	Volume	
	g/mol	wt-%	mol	g	l or ml	
Pb3O4	685.598	100	1	685.598	76.861	ml
	g/mol	wt-%	mol	g	l or ml	
PbO	223.199	97.666	3	669.598	70.262	ml
O2(g)	31.999	2.334	0.5	15.999	11.207	l

Pb3O4= 3PbO + 0.5O2(g)

T	deltaH	deltaS	deltaG	K	Log(K)
C	kJ	J/K	kJ		
0	64.528	96.8	38.088	5.20E-08	-7.284
100	63.967	95.14	28.465	1.04E-04	-3.985
200	62.6	91.921	19.108	7.77E-03	-2.11
300	60.864	88.598	10.084	1.21E-01	-0.919
400	59.046	85.674	1.375	7.82E-01	-0.107
500	57.291	83.242	-7.068	3.00E+00	0.478
600	55.578	81.159	-15.285	8.21E+00	0.914
700	53.889	79.327	-23.308	1.78E+01	1.251
800	52.211	77.685	-31.157	3.29E+01	1.517

900	127.316	142.437	-39.783	5.91E+01	1.772
1000	126.917	142.113	-54.013	1.65E+02	2.216
1100	126.116	141.509	-68.197	3.93E+02	2.594
1200	124.91	140.663	-82.307	8.29E+02	2.919

Formula	FM g/mol	Conc. wt-%	Amount mol	Amount g	Volume l or ml	
Pb3O4	685.598	100	1	6.86E+02	76.861	ml
	g/mol	wt-%	mol	g	l or ml	
PbO	223.199	97.666	3	669.598	70.262	ml
O2(g)	31.999	2.334	0.5	15.999	11.207	l
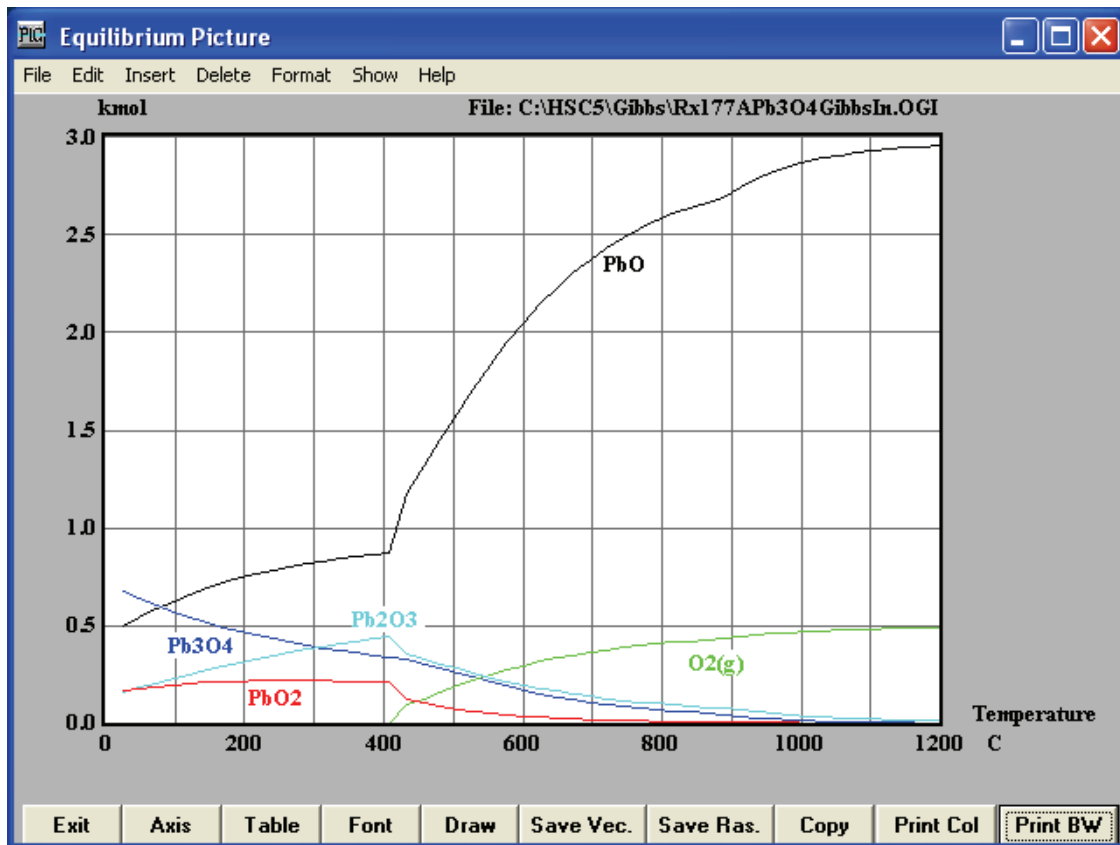
Fig. 1. Reaction 177A equilibrium picture (from Ref. [2]).

TABLE 2 – REACTION 177B DELTA G CALCULATIONS (FROM REF. 2)

Reaction 177B is spontaneous from 0 to 1893°C (2166 K) where delta G = 0
From CRC Handbook: m.p. PbCl2 = 501°C, b.p. PbCl2 = 950°C
Reaction 177B Temp = 400°C (per Ref. 1)
6HCl + 3PbO = 3PbCl2(s) + 3H2O
6HCl(g) + 3PbO = 3PbCl2 + 3H2O(g)
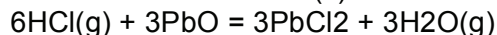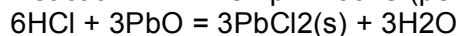
T	deltaH	deltaS	deltaG	K	Log(K)
C	kJ	J/K	kJ		
1880	-478.926	-221.089	-2.887	1.18E+00	0.07
1881	-478.846	-221.052	-2.666	1.16E+00	0.065
1882	-478.766	-221.015	-2.445	1.15E+00	0.059
1883	-478.686	-220.978	-2.224	1.13E+00	0.054
1884	-478.606	-220.941	-2.003	1.12E+00	0.049
1885	-478.527	-220.904	-1.782	1.10E+00	0.043
1886	-478.447	-220.867	-1.561	1.09E+00	0.038
1887	-478.367	-220.83	-1.34	1.08E+00	0.032
1888	-478.287	-220.793	-1.12	1.06E+00	0.027
1889	-478.207	-220.756	-0.899	1.05E+00	0.022
1890	-478.127	-220.719	-0.678	1.04E+00	0.016
1891	-478.047	-220.683	-0.457	1.03E+00	0.011
1892	-477.968	-220.646	-0.237	1.01E+00	0.006
> 1893	-477.888	-220.609	-0.016	1.00E+00	0
1894	-477.808	-220.572	0.205	9.89E-01	-0.005
1895	-477.728	-220.535	0.425	9.77E-01	-0.01
1896	-477.648	-220.498	0.646	9.65E-01	-0.016
1897	-477.568	-220.461	0.866	9.53E-01	-0.021
1898	-477.488	-220.425	1.087	9.42E-01	-0.026
1899	-477.408	-220.388	1.307	9.30E-01	-0.031
1900	-477.328	-220.351	1.527	9.19E-01	-0.037

PbO   Extrapolated from   2000 K

Formula	FM	Conc.	Amount	Amount	Volume	
	g/mol	wt-%	mol	g	l or ml	
HCl(g)	36.461	24.626	6	2.19E+02	134.482	l
PbO	223.199	75.374	3	6.70E+02	70.262	ml
	g/mol	wt-%	mol	g	l or ml	
PbCl2	278.106	93.916	3	8.34E+02	139.518	ml
H2O(g)	18.015	6.084	3	5.40E+01	67.241	l

6HCl(g) + 3PbO = 3PbCl2 + 3H2O(g)

T	deltaH	deltaS	deltaG	K	Log(K)
C	kJ	J/K	kJ		
0	-596.143	-354.789	-499.233	3.00E+95	95.477
100	-594.1	-348.426	-464.085	9.32E+64	64.969
200	-591.733	-342.827	-429.525	2.65E+47	47.422
300	-588.865	-337.345	-395.516	1.12E+36	36.049
400	-585.456	-331.874	-362.055	1.25E+28	28.097
500	-581.511	-326.418	-329.141	1.73E+22	22.239

600	-505.737	-229.283	-305.539	1.91E+18	18.28
700	-495.938	-218.653	-283.155	1.58E+15	15.2
800	-486.495	-209.414	-261.762	5.52E+12	12.742
900	-554.157	-267.532	-240.302	5.02E+10	10.7
1000	-546.7	-261.431	-213.859	5.96E+08	8.775
1100	-539.245	-255.794	-188.001	1.42E+07	7.152
1200	-531.721	-250.506	-162.688	5.88E+05	5.769
1300	-524.134	-245.523	-137.889	3.79E+04	4.579
1400	-516.487	-240.811	-113.575	3.52E+03	3.546
1500	-508.779	-236.336	-89.719	4.40E+02	2.643
1600	-501.011	-232.075	-66.3	7.06E+01	1.849
1700	-493.181	-228.003	-43.298	1.40E+01	1.146
1800	-485.288	-224.1	-20.694	3.32E+00	0.521
1900	-477.328	-220.351	1.527	9.19E-01	-0.037
2000	-469.3	-216.739	23.381	2.90E-01	-0.537

PbO   Extrapolated from   2000   K

Formula	FM g/mol	Conc. wt-%	Amount mol	Amount g	Volume l or ml	
HCl(g)	36.461	24.626	6	218.765	134.482	l
PbO	223.199	75.374	3	669.598	70.262	ml
	g/mol	wt-%	mol	g	l or ml	
PbCl2	278.106	93.916	3	834.318	139.518	ml
H2O(g)	18.015	6.084	3	54.046	67.241	l

6HCl(g) + 3PbO = 3PbCl2 + 3H2O(g)
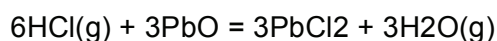
T C	deltaH kJ	deltaS J/K	deltaG kJ	K	Log(K)
1800	-485.288	-224.1	-20.694	3.32E+00	0.521
1810	-484.495	-223.719	-18.455	2.90E+00	0.463
1820	-483.701	-223.339	-16.22	2.54E+00	0.405
1830	-482.907	-222.96	-13.988	2.23E+00	0.347
1840	-482.112	-222.583	-11.76	1.95E+00	0.291
1850	-481.316	-222.208	-9.536	1.72E+00	0.235
1860	-480.52	-221.833	-7.316	1.51E+00	0.179
1870	-479.723	-221.461	-5.1	1.33E+00	0.124
1880	-478.926	-221.089	-2.887	1.18E+00	0.07
1890	-478.127	-220.719	-0.678	1.04E+00	0.016
1900	-477.328	-220.351	1.527	9.19E-01	-0.037

PbO   Extrapolated from   2.00E+03   K

| Formula	FM g/mol	Conc. wt-%	Amount mol	Amount g	Volume l or ml	
HCl(g)	36.461	24.626	6	2.19E+02	134.482	l
PbO	223.199	75.374	3	669.598	70.262	ml
	g/mol	wt-%	mol	g	l or ml	
PbCl2	278.106	93.916	3	834.318	139.518	ml
H2O(g)	18.015	6.084	3	54.046	67.241	l

Fig. 2. Reaction 177B equilibrium picture (from Ref. [2]).

TABLE 3. REACTION 177C DELTA G CALCULATIONS (FROM REF. [2])
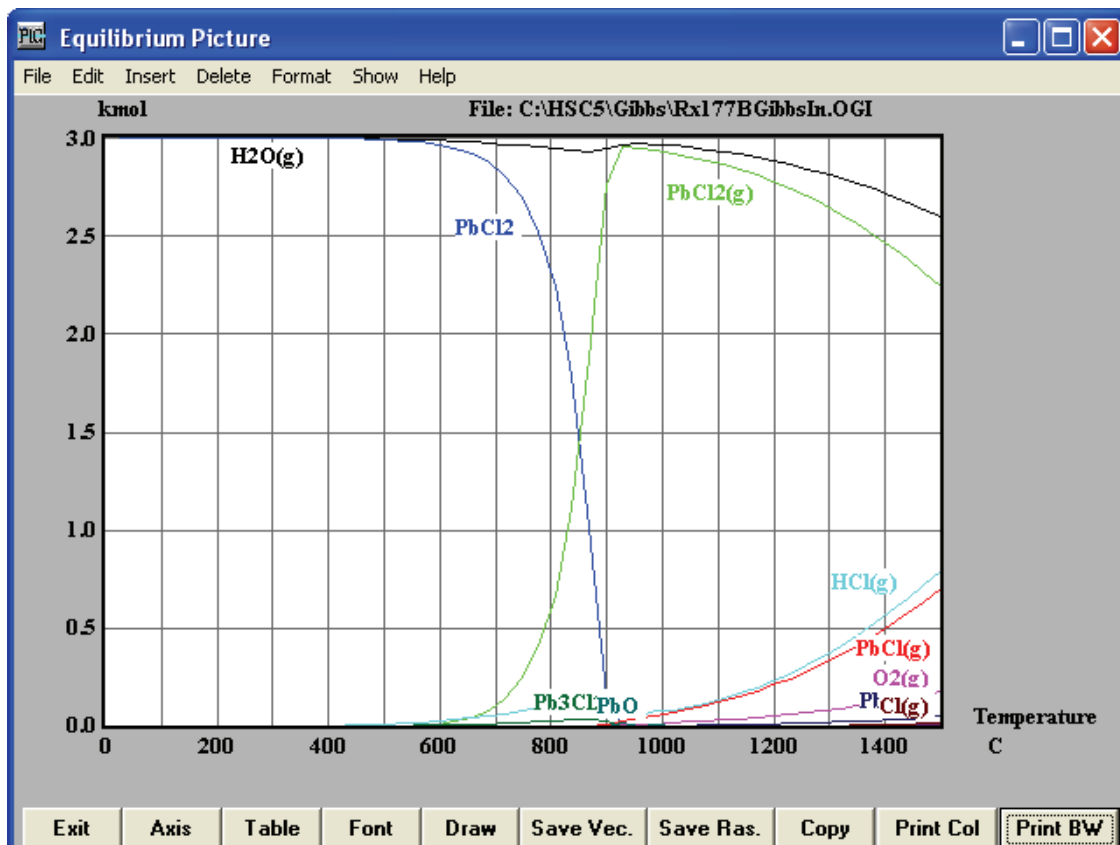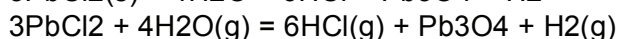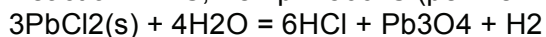
Reaction 177C is nonspontaneous from 0 to 3000°C
From CRC Handbook: Pb3O4 decomposes at 500°C;
   m.p. PbCl2 = 501°C, b.p. PbCl2 = 950°C
Reaction 177C, Temp = 500°C (per Ref. 1)
3PbCl2(s) + 4H2O = 6HCl + Pb3O4 + H2
3PbCl2 + 4H2O(g) = 6HCl(g) + Pb3O4 + H2(g)

T	deltaH	deltaS	deltaG	K	Log(K)
C	kJ	J/K	kJ		
0	773.196	301.553	690.827	7.62E-133	-132.118
100	772.7	299.924	660.783	3.12E-93	-92.506
200	772.641	299.783	630.799	2.27E-70	-69.645
300	772.413	299.355	600.837	1.73E-55	-54.762
400	771.684	298.197	570.952	4.92E-45	-44.308
500	770.312	296.307	541.222	2.70E-37	-36.568
600	697.016	202.187	520.477	7.26E-32	-31.139
700	689.611	194.154	500.669	1.33E-27	-26.876
800	682.485	187.182	481.61	3.60E-24	-23.444
900	675.607	181.053	463.205	2.37E-21	-20.626
1000	669.041	175.679	445.375	5.32E-19	-18.274
1100	662.814	170.969	428.047	5.20E-17	-16.284
1200	656.864	166.786	411.164	2.63E-15	-14.58
1300	651.203	163.066	394.675	7.84E-14	-13.106
1400	645.838	159.759	378.537	1.52E-12	-11.819
1500	640.777	156.821	362.711	2.06E-11	-10.686
1600	636.024	154.212	347.162	2.08E-10	-9.682
1700	631.581	151.9	331.858	1.64E-09	-8.786
1800	627.451	149.858	316.773	1.04E-08	-7.982
1900	623.635	148.06	301.879	5.54E-08	-7.257
2000	620.134	146.484	287.153	2.52E-07	-6.599
2100	616.949	145.113	272.575	1.00E-06	-6
2200	614.082	143.929	258.124	3.53E-06	-5.452
2300	611.546	142.923	243.783	1.12E-05	-4.949
2400	609.355	142.088	229.534	3.27E-05	-4.486
2500	607.522	141.414	215.36	8.77E-05	-4.057
2600	606.055	140.894	201.246	2.19E-04	-3.659
2700	604.957	140.518	187.177	5.14E-04	-3.289
2800	604.228	140.276	173.138	1.14E-03	-2.943
2900	603.871	140.161	159.117	2.40E-03	-2.62
3000	603.886	140.166	145.102	4.83E-03	-2.316
PbCl2		Extrapolated from		2300	K
Pb3O4		Extrapolated from		2000	K

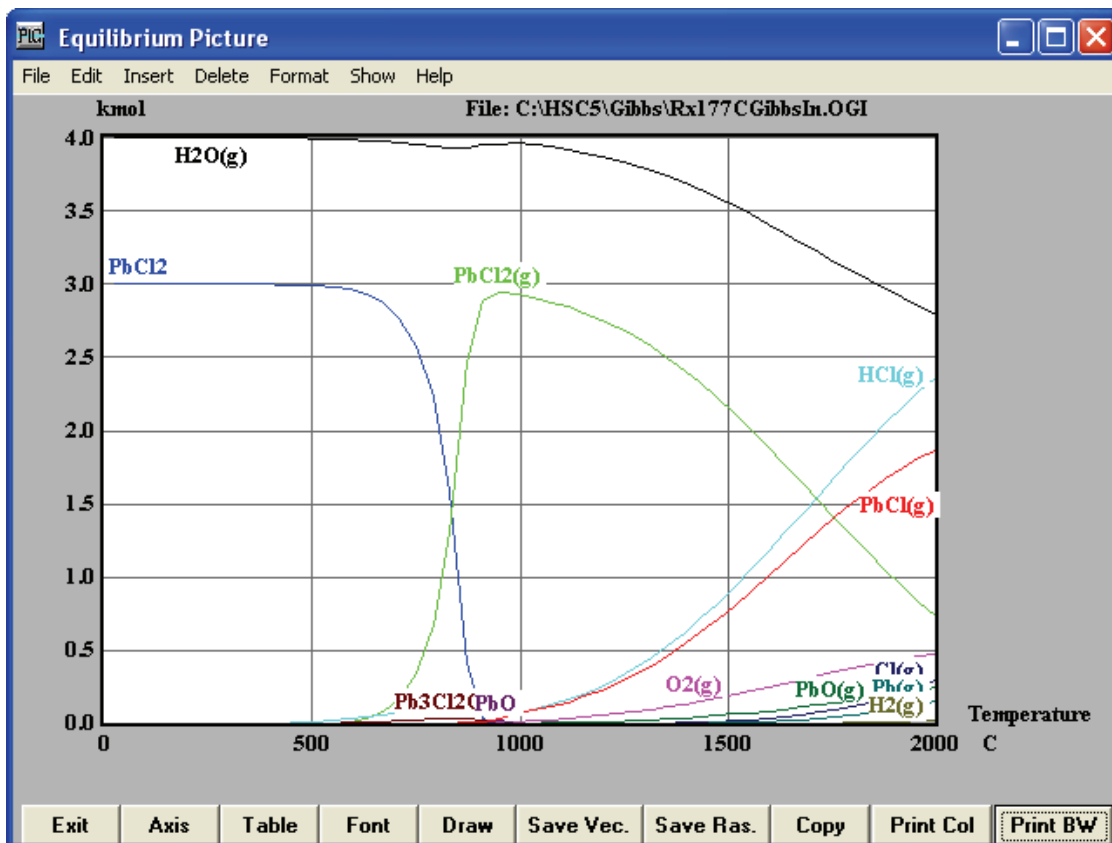| Formula	FM	Conc.	Amount	Amount	Volume	
	g/mol	wt-%	mol	G	l or ml	
PbCl2	278.106	92.05	3	8.34E+02	139.518	ml
H2O(g)	18.015	7.95	4	7.21E+01	89.654	l
	g/mol	wt-%	mol	G	l or ml	
HCl(g)	36.461	24.136	6	2.19E+02	134.482	l
Pb3O4	685.598	75.641	1	6.86E+02	76.861	ml
H2(g)	2.016	0.222	1	2.02E+00	22.414	l

A2-169

Fig. 3. Reaction 177C equilibrium picture (from Ref. [2]).

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 182 – CADMIUM CARBONATE

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (°C)
Cd-2	$Cd(s) + CO_2(g) + H_2O(l) = CdCO_3 + H_2(g)$	1	25
CdCO3	$CdCO_3 = 2CO_2 + 2CdO(s)$	0.5	300
CdO	$2CdO = Cd + O_2(g)$	0.5	1200

SUMMARY

This cycle is not technically feasible at a maximum temperature of 1200°C. With heat recovery and batch operation, efficiency is about 52.4% if a solar heater can provide 1600°C to the CdO reactor, and operating costs may be $30/mole of H2 for inert gas consumption in addition to other operating costs.

DISCUSSION

Cd-2 REACTOR

This reaction is unique to this cycle. HSC-5 data for the exothermic Cd-2 reaction indicate that delta G is negative below 343 C, with fast kinetics at 100°C, where pressure can facilitate dissolving $CO_2(g)$ in water. The reactor requires rejecting 83 MJ per kg of H2 produced at 100°C and does not appear to be a good candidate for an electrochemical step.

CdCO3 REACTOR

This reaction is unique to this cycle. HSC-5 data for the endothermic CdCO3 reaction show delta G is negative above 295°C, with good kinetics at 400°C. The maximum duty for the reactor is 127 MJ for discharge at the proposed temperature per kg mole of H2 with dry feed. A lower temperature and/or a counter-flow heat exchanger would not significantly reduce this duty.

CdO REACTOR

This reaction is common to PID 5 and 182. HSC-5 data for the CdO reaction show delta G < 0 above 1551°C, just below where CdO is a gas. The reverse reaction is highly favored below that temperature. Testing indicated that the reaction could be completed in a stream of inert carrier gas such as argon between 1350 and 1610°C [1]. The carrier gas was necessary to drive the reaction and sweep the oxygen from the reactor before it oxidized the Cd that was produced as a coating on a water-cooled condenser. When counter-flow input-output heat exchanger is used for the argon and oxygen, the duty for this reactor is 418 MJ per mole of H2 at 1600°C plus heat leak from this reactor, assuming one mole of argon is used.

The carrier gas cannot easily be separated from oxygen for recycle to the CdO reactor, so operating costs should reflect purchase of at least one mole of Ar per mole of H2 produced at a cost of about $30/mole. The reactor would have to be operated in batch mode to provide a means for separating and removing Cd metal from the water-cooled condenser.

Rewriting the reaction table to match the required conditions results in the following table:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Cd-2	$Cd(s) + CO2(g) + H2O(l) = CdCO3(s) + H2(g)$	1	100
CdCO3	$CdCO3(s) = 2CO2(g) + 2CdO(s)$	0.5	400
CdO	$2CdO(g) = Cd(g) + O2(g)$	0.5	1600

This assessment resulted in the following conclusions:

This cycle is not technically feasible at a maximum temperature of 1200°C. With heat recovery and batch operation, efficiency is about 52.4% if a solar heater can provide 1600°C to the CdO reactor, and operating costs may be $30/mole of H2 for inert gas consumption in addition to other operating costs.

REFERENCES

[1] Whaley, T., Yudow, B., Remick, R., Pangborn, J., Sammells, A., "Status of the Cadmium Thermoelectrochemical Hydrogen Cycle," *Int. J. Hydrogen Energy,* Vol. **8**, No. 10, pp. 767-771. 1983.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 184 – HYBRID ANTIMONY-BROMINE

This hybrid process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Br2-9	2Br2(l) + Sb2O3(s) + 2H2O(l) = 4HBr(aq) + Sb2O5(s)	0.5	80
HBr-2	2HBr = Br2 + H2(g)	1	100
Sb2O5	Sb2O5 = Sb2O3 + O2(g)	0.5	1000

SUMMARY

The thermal efficiency of this cycle is 29.6% when the electric power for the HBr electrolyzer is charged at 38% efficiency for the electric generator. If the generator is 50% efficient, the cycle efficiency is 36.2%.

DISCUSSION

Br2-9 REACTOR

Delta G is negative for all temperatures for this exothermic reaction. When reactants are fed at the temperatures required for separation of O2 and Br2 distillation, the heat balance for this reactor requires a cooler with a cooling duty of 174 MJ/kg-mole of H2 produced.

HBr-2 REACTOR

Delta G is positive for all temperatures for this reaction, so an electrolyzer is proposed, operating at 100°C. The heat balance for the reactor shows that 275 MJ/kg-mole of H2 is required in the electrolyzer.

Sb2O5 REACTOR

Delta G is negative above 844°C for this reaction. Operation at 1000°C should provide adequate kinetics and an inlet/outlet counter-flow heat exchanger with 10°C approach can minimize solar energy required to 190 MJ/kg-mole of H2.

A flowsheet (Fig. 1) and M&EB (Table 1) show the proposed equipment, the flow rates and conditions for delivery of H2 at 50 bar.

The thermal efficiency of this cycle is 29.6% when the electric power for the HBr electrolyzer is charged at 38% efficiency for the electric generator. If the generator is 50% efficient, the cycle efficiency is 36.2%.

System Thermal Efficiency = | 29.6% | = (HHV of H2) / (Total solar heat input)

H2O(l)   ◇1

Sb2O5 reactor chemistry

1/2Sb2O5 = 1/2Sb2O3 + 1/2O2(g)

◇4

Solar duty 190 MJ

Sb2O5 reactor 1000 C

◇14   HX   ◇13

◇15   Cooler

Oxygen separator   ◇3   O2(g)

◇16

Br2-9 reactor chemistry

Br2(a) + 1/2Sb2O3 + H2O(l) = 2HBr(ia) + 1/2Sb2O5

◇5   H2(g)

Br2-9 reactor 80 C

Cooler duty = 174 MJ

Filter   ◇11

◇12   Pump

◇10   Br2 distillation   Solar duty 40 MJ

◇7

◇6

HBr-2 reactor chemistry

2HBr(ia) = Br2(a) + H2(g)

◇2   Hydrogen washer

Pump

HBr-2 reactor 100 C aqueous electrol yzer

Electricity2 80 MJ

◇8

◇9   Pump
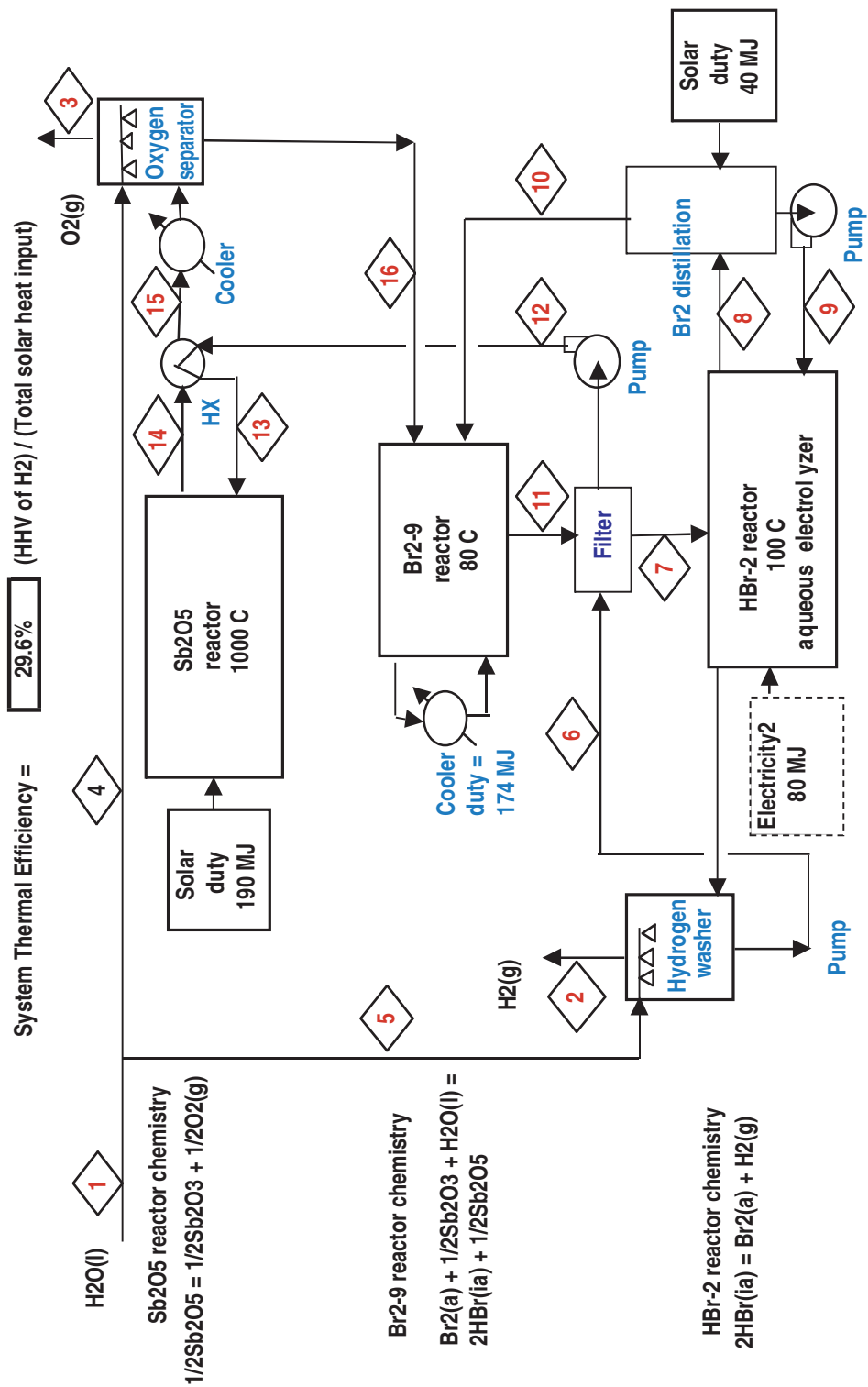
Fig. 1. PID 184 flowsheet.

TABLE 1. PID 184 — OR671 MASS BALANCE

Stream	1	2	3	4	5	6	7	8	9	10	11	12
Description	Water to plant	Hydrogen	Oxygen	Water to O2 separator	Water to H2 washer	Water to Sb2O3 filter	HBr solution to electrolyzer	Br2 solution to distillation	Water from Br2 distillation	Br2 solution from Br2 distillation	Br2 reactor products to filter	Sb2O5 filter cake to HX
Temperature, °C	25	30	60	25	25	79	80	100	100	100	80	80
Pressure (absolute), bar	53	50	50	53	53	49	51	51	51	50	49	53
Volume, normal cu. m.		22.91	11.40									
GPM												
Volume, actual cu. m.	0.02	0.47	0.25	0.01	0.01	0.01	0.26	1.92	1.72	0.21	0.47	0.29
Gases												
H2(g)		2.02										
H2O(g)												
O2(g)			16.00									
Total gases	0.00	2.02	16.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Liquids & Solutions												
Br2(a)								159.81			161.82	
HBr(ia)												
Sb2O3(l)												
H2O(l)	18.02			9.01	9.01	9.01	198.17	1855.55	1657.38	198.17	369.31	180.15
Total liquids/solutions	18.02	0.00	0.00	9.01	9.01	9.01	198.17	2015.35	1657.38	198.17	531.13	180.15
Solids												
Sb2O3												
Sb2O5											161.75	161.75
Total solids	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	161.75	161.75
Total gases, liquids & solids	18.02	2.02	16.00	9.01	9.01	9.01	198.17	2015.35	1657.38	198.17	692.88	341.90

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 185 – HYBRID COBALT BROMIDE-2

This process is based on the following chemical reactions in the UNLV database, where no references are listed:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Br2-10	$Br_2(g) + 4CoO(s) = CoBr_2(s) + Co_3O_4(s)$	1	500
Co3O4	$2Co_3O_4(s) = 6CoO(s) + O_2(g)$	0.5	900
CoBr2	$CoBr_2(l) + H_2O(g) = 2HBr + CoO(s)$	1	750
HBr-4	$4HBr(aq) = 2Br_2(aq) + 2H_2(g)$	0.5	25

SUMMARY

The calculated cycle efficiency for PID 185 is 25.6% at 50% source efficiency and 22.0% at 38% source efficiency. Therefore, this cycle does not warrant further development.

DISCUSSION

Br2-10 REACTOR

This exothermic reaction is unique to this PID and delta G < 0 below 603°C. K = 289.5 at 500°C and 350 MJ per kg-mole of H2 produced must be removed to maintain 500°C in the reactor. This heat can be used to raise steam for the CoBr2 reactor, but the rest must be rejected.

Co3O4 REACTOR

This endothermic reaction was also proposed in PIDs 84, 88, and 150, none of which are proposed for Phase II assessment. HSC-5 data show that delta G is negative above 937°C; however, equilibrium data show 1 mole of Co3O4 remains at about 970°C and does not disappear at 1 bar pressure until about 1500°C is reached, and over 1600°C is required at 50 bar. A 1300°C low-pressure solar-heated moving bed reactor is required to minimize Co3O4 carryover to the Br2-10 reactor with a duty of 360 MJ per kg-mole of H2 produced.

CoBr2 REACTOR

This endothermic reaction was also proposed in PID 174, which was not proposed for Phase II assessment. HSC-5 data show that delta G is negative above 678°C, where CoBr2 is liquid. The solar duty for operation at 750°C would be 175 MJ per kg-mole of H2 produced.

HBr-4 REACTOR

This electrochemical reaction was also proposed in PID 189, which was not proposed for Phase II assessment. The proposed operating temperature of 25°C appears to be required to maintain the Br2 aqueous, while releasing the H2(g) at pressure. This approach requires cooling and a distillation step to prepare Br2(g) for introduction to the Br2-10 reactor. Electrochemical operation will require 290 MJ of electrical energy in the reactor and 580 MJ at 50% source efficiency, or 763 MJ at 38% source efficiency.

The calculated cycle efficiency for PID 185 is 25.6% at 50% source efficiency and 22.0% at 38% source efficiency. Therefore, this cycle does not warrant further development.

UNLV Solar Thermal Hydrogen Generation Project, DOE

PID 191 – HYBRID COPPER CHLORIDE

This process is based on the following chemical reactions in the UNLV database [1]:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Cu	$2Cu + 2HCl = 2CuCl + H_2(g)$	1	430
CuCl2-1	$4CuCl_2(s) + 2H_2O = 4CuCl(l) + 4HCl + O_2$	0.5	550
CuCl-5	$4CuCl(aq) = 2Cu + 2CuCl_2(aq)$	1	75

SUMMARY

The resulting efficiency, including the electrical input for the electrochemical CuCl-5 reaction step, is 45.2% at a source efficiency of 38% and 49.2% at a source efficiency of 50%. Further evaluation is recommended.

DISCUSSION

Cu REACTOR

When HCl is assumed to be gas, delta G for the Cu reaction is negative below 464°C. The melting point for CuCl is 430°C, so operating the reactor below that temperature would be beneficial, where the reaction kinetics are better. HSC-5 equilibrium data show that about 0.4 moles of HCl remains in the reactor effluent at 400°C that is introduced to the CuCl-5 reactor. A gas transport reactor was assumed for this assessment operating at 400°C, where the solar energy requirement is 90 MJ per kg-mole of H2 produced. A counter-flow heat recovery boiler is used to heat and evaporate the Cu/HCl water slurry, which significantly lowers the solar energy required.

CuCl2-1 REACTOR

Delta G for the CuCl2-1 reaction is negative above 590°C, so only a higher temperature than proposed will produce oxygen. The melting points for CuCl and CuCl2 are 430 and 598°C respectively, so a transport reactor could be used above 600 C where the reaction kinetics are better. A temperature of 700° was selected for this assessment, where the solar energy required is 325 MJ per kg-mole of H2 produced. A counter-flow heat recovery boiler is used to heat and evaporate the CuCl2 water slurry, which significantly lowers the solar energy required.

CuCl-5 REACTOR

Delta G for the CuCl-5 reaction is positive at all temperatures, so an electrochemical step is proposed [1]. This approach requires CuCl(aq), but the solubility in water at 25°C is negligible and no means of dissolving the CuCl is specified. About 0.4 moles of HCl remains in the Cu

reactor effluent at 400°C that can dissolve CuCl in the CuCl-5 reactor. A membrane is required to separate unreacted CuCl solution from CuCl2 solution for discharge. A Pourbaix diagram shows a very limited region of pH from -1 to +4 where CuCl2 is stable in an electrochemical environment [2]. The electrical energy requirement is 83 kJ, and the source energy requirement is 166 MJ at 50% source efficiency and 218 MJ at 38% source efficiency.

The flow diagram (Fig. 1) and mass balance (Table 1) incorporate these changes, as represented by the following reactions:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
Cu	$2Cu(s) + 2HCl(g) = 2CuCl(s) + H_2(g)$	1	400
CuCl2-1	$4CuCl2(l) + 2H_2O(g) = 4CuCl(l) + 4HCl(g) + O_2(g)$	0.5	700
CuCl-5	$4CuCl(a) = 2Cu(s) + 2CuCl2(a)$	1	75 (electrochemical)

The flows include water to dissolve the CuCl2 and discharge a 50% moisture filter cake from the CuCl-5 reactor. A cooler and two heat exchangers minimize energy requirements so that the solar duty is only 415 MJ per kg-mole of H2 produced.

The resulting efficiency, including the electrical input for the electrochemical CuCl-5 reaction step, is 45.2% at a source efficiency of 38% and 49.2% at a source efficiency of 50%. Further evaluation is recommended.

REFERENCES

[1]   Lewis, M., "Low-Temperature Thermochemical Generation of Hydrogen from Water," http://www.cmt.anl.gov/science-technology/lowtempthermochemical.shtml

[2]   Scott, D., "The Reactions of Cuprous Chloride," http://aic.stanford.edu/jaic/articles /jaic29-02-007_3.html

System Thermal Efficiency = $\boxed{45.2\%}$ (HHV of H2) / (Total solar heat input)

H₂O(l)

O2(g)

H₂O(l)

Oxygen separator

Cu reactor chemistry
2Cu(s) + 2HCl(g) =
2CuCl(s) + H2(g)

Solar Heater
140 MJ

CuCl2-1 reactor chemistry

2CuCl2(l) + H₂O(g) = 2CuCl(l) +
2HCl(g) + 1/2O₂(g)

CuCl-5 reactor chemistry

4CuCl(a) = 2Cu(s) + 2CuCl2(a)

Solar
duty
90 MJ

Cu
transport reactor
400 C pressurized

Cooler

Heat Recovery Boiler B

H2O(l)

Solar
duty
325 MJ

CuCl2-1
Reactor
700 C

Heat Recovery Boiler A

Pump

liquid CuCl cooler

Electricity2
18 MJ

CuCl-5 Reactor
75 ˚C
Aqueous Electrolyzer

Pump

Filter

1 2 3 4 5 6 7 8 9 10 12 13 14 15 16 17 18

Fig. 1 – PID 191 flow diagram.

A2-180

TABLE 1. PID 191 MASS BALANCE

PID 191 - ANL Copper Chloride

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Description	Water to plant	Hydrogen	Oxygen	Water to O2 separator	Hydrochloric from O2 separator	Hydrochloric acid & copper to CuCL Coller	Hydrochloric acid & copper to HRB B	Hydrochloric acid vapor to Cu reactor	CuCl & H2 in steam to HRB B	CuCl & H2 in water to cooler	CuCl in water to CuCl-5 reactor	Copper filter cake	CuCl solution to HRB A	Steam & CuCl2 to Cucl2-1 reactor	CuCl2-1 reactor offgas to HRB A	CuCl solution to O2 separator	Liquid CuCl to cooler	CuCl to CuCl-5 reactor
Temperature,	25	60	60	25	83	79	115	260	400	125	65	75	75	597	700	85	700	90
Pressure (absolute), bar	54	51	46	54	51	50	49.5	48	48	47	46	51	53	52	52	51	52	46
Volume, normal cu. m.		22.91	11.40				706.78	706.78	684.16	23.49				336.20	60.83	11.40		
GPM Volume, actual cu. m.	0.02	0.50	0.28	0.01	0.25	0.54	18.59	26.34	32.24	1.23	0.54	0.29	0.27	18.95	3.82	0.52	0.05	0.05
Gases																		
H2(g)		2.02							2.02	2.02								
HCl(g)							72.92	72.92							72.92			
H2O(g)							531.45	531.45	531.45					270.23	252.21			
O2(g)			16.00												16.00	16.00		
Total Gases	0.00	2.02	16.00	0.00	0.00	0.00	604.37	604.37	533.46	2.02	0.00	0.00	0.00	270.23	341.13	16.00	0.00	0.00
Liquids & Solutions																		
CuCl2(a)													268.90					
CuCl(l)									198.00								198.00	198.00
CuCl(a)											198.00							
HCl(a)					72.92	72.92										72.92		
H2O(l)	18.02			9.01	261.22	531.45				531.44	540.45	270.23	270.23			252.21		
Total liquids/solutions	18.02	0.00	0.00	9.01	334.14	604.37	0.00	0.00	198.00	531.44	738.45	270.23	539.13	0.00	0.00	325.13	198.00	198.00
Solids																		
CuCl2(s)														268.90				
CuCl(s)										198.00								
Cu(s)						127.09	127.09	127.09				127.09						
Total solids	0.00	0.00	0.00	0.00	0.00	127.09	127.09	127.09	0.00	198.00	0.00	127.09	0.00	268.90	0.00	0.00	0.00	0.00
Total gases, liquids & solids	18.02	2.02	16.00	9.01	334.14	731.46	731.46	731.46	731.46	731.46	738.45	397.32	539.13	539.13	341.13	341.13	198.00	198.00

PID 193 – MULTIVALENT SULFUR-3

This process is based on the following chemical reactions from Ref. [1]:

Reaction No.	Reaction Code	Formula	Multiplier	Max. Temp. (°C)
193D	H2S	2H2S = S2 + 2H2(g)	0.5	1570
193A	H2SO4	2H2SO4(g) = 2SO2(g) + 2H2O(g) + O2(g)	0.5	850
193C	S2	3S2(g) + 4H2O = 4H2S + 2SO2	0.25	490
193B	SO2-4	3SO2(g) + 2H2O(l) = 2H2SO4(a) + S(s)	0.5	150

SUMMARY

The maximum thermal efficiency from the PID 193 cycle is predicted to be 42.2%.

Discussions of each reaction along with a simplified flowsheet for this cycle (Fig. 1) are shown below

REACTOR 193A

Calculations using Ref. [2] show that reaction 193A is spontaneous at temperatures above 785°C, where delta G is zero. The 850°C maximum temperature specified in Ref. [1] for this reaction is sufficient. An 850°C operating temperature can be maintained with a 336.22 MJ solar heater.

The Reactor 193A offgas mixture is cooled to 5°C in Steam Condenser 193A. For this assessment, all of the heat in this Condenser is rejected.

Following cooling, the gases are compressed, and cooled in SO2 Condenser 193A to liquefy the SO2. The O2 is scrubbed with 0.5 mole feed H2O, and is removed as product. The liquid SO2 is fed with the H2O from the scrubbers into Reactor 193B.

Although calculations using Ref. 2 indicate that the SO2 + O2 offgas mixture from Reactor 193A will react to form SO3 when cooled below 32°C, a catalyst is required to promote this reaction. Also, when the SO2 is cooled to a 5°C gas and condensed to a liquid, it's dwell time as a cold gas is brief.

REACTOR 193B

The equilibrium for reaction 193B lies to the right at temperatures below 128°C. The 150°C temperature specified for reaction 193B is too high. A 25°C temperature was selected for this assessment. The H2SO4 and S exiting Reactor 193B can be separated by filtration and

transferred to Reactors 193A and 193C. The heat content in the reactants plus the 44.16 MJ exotherm from reaction 193B requires a 12.84 MJ cooler to maintain 25°C in the reactor.

REACTOR 193C

If the H2O reactant is specified as a gas, reaction 193C is spontaneous at temperatures below 492°C, where delta G is zero. The 490°C maximum temperature specified in Ref. [1] for this reaction is near the maximum. The boiling point of sulfur is 445°C. A 460°C temperature was selected for this assessment to allow more margin below the delta G = 0 temperature with S2 and H2O as reactant gasses. It should be noted that when the physical state of the H2O reactant is not specified in the Ref. [2] equation for reaction 193C, delta G is negative from 0 to 1000°C.

The H2S and SO2 reaction product gases from Reactor 193C are cooled to 25°C, and the SO2 is scrubbed from the H2S with feed H2O. The H2S is transferred to Reactor 193D.

REACTOR 193D

In Reactor 193D, the H2S is decomposed into S2 and H2 gases at temperatures above 1564°C where delta G =0. The 1570°C temperature specified for this reaction was increased to 1600°C for this assessment to achieve a higher equilibrium constant.

The gaseous reaction products from this reactor are cooled, and the sulfur is liquefied and separated from the H2. The liquid sulfur is pumped to Reactor 193C as a reactant.

The H2 is scrubbed with feedwater and transferred to product storage.

SUMMARY

The maximum thermal efficiency from the PID 193 cycle is predicted to be 42.2%. Although this is sufficiently high to justify a more rigorous evaluation, process design would be complicated by slow kinetics and difficult separations.

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[1]   UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.
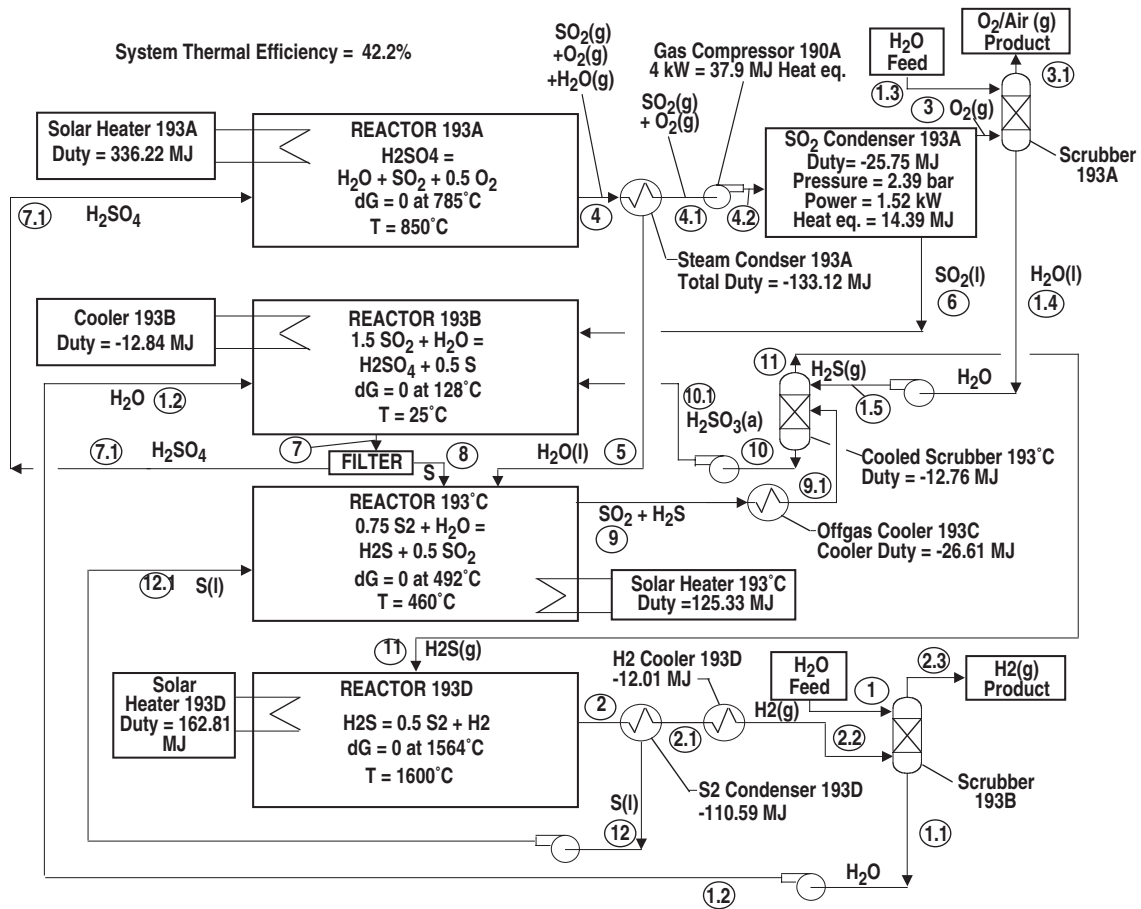
Fig. 1. PID 193 flowsheet.

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PID194- ZINC-MANGANESE FERRITE

The Fe Mn Zn Ferrite cycle is based on the following two reactions from Ref. [1]. This cycle is related to PIDs 2, 7, and 152.

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
MnFe2O4-1	MnFe2O4(s) + 3 ZnO(s) + H2O(g) = Zn3MnFe2O8(s) + H2	1	1000
Zn3MnFe2O8	2Zn3MnFe2O8(s) = 2MnFe2O4(s) + 6 ZnO(s) + O2	0.5	1200

For Fe_2ZnO4 dissociation calculations using HSC, Ref. [2], indicate a zero delta G between 2300 and 2400 K, substantially lower than for dissociation of Fe_3O_4, which is over 3100. The HSC database does not include the zinc, manganese, ferrite in the database, so it is difficult to assess the potential of this cycle. HSC only accounts for pure substances and does not account for solid solutions, which could lower the oxygen releasing reaction temperature. HSC, however, does indicate that mixed metal oxides of iron with manganese and/or zinc can reduce the dissociation temperature. Tables 1 and 2, below for the reduction and hydrolysis of zinc ferrite, respectively suggest temperatures close to 2000 K might be feasible. There has been a great deal of theoretical and laboratory research in Japan and Europe that suggests that reduction temperatures for mixed metal oxides can be substantially reduced, compared to iron oxide alone. Much of the recent work has been on zinc ferrites (Refs. [3–6])

Although much of the high temperature reduction work has been done at temperatures as low as 1300 K, they were typically conducted with a flowing inert gas, effectively reducing the oxygen partial pressure to essentially zero. Activating redox sites in the manganese ferrite spinel is suggested as the mechanism for enhanced oxygen generation at reduced temperatures. However, calculations with HSC, assuming all of the likely species, indicate temperature of over 2000K are required to get substantial oxygen production. Figures 1 and 2 show the equilibrium products after iteratively reducing a mixture that starts with one mole of Fe_2MnO_4 and 1 mole of ZnO, heating it to 2100K at 1 bar, removing the oxygen, cooling it to 600K, reacting it with 1 mole of H2O(g) at 1 bar, removing the hydrogen, heating it to 2100 K, removing the oxygen, etc. Table 3 shows the resulting compositions assuming equilibrium at the output of the two reactors at 1 bar. These results indicate a reaction extent of about 25%, or 0.25 moles H_2 per mole of Fe_2MnO_4 plus 1 mole of ZnO. If the equilibrium can be shifted by virtue of mixed metal oxides, or reducing pressure or removing products to shift the reaction, then higher reaction extents or lower reaction temperatures may be possible.

Table 1. Thermodynamics of $Fe_2ZnO_4 = 2FeO + ZnO + 1/2O_2(g)$

T	deltaH	deltaS	deltaG	K
K	kcal	cal/K	kcal	
1000.000	69.086	27.518	41.568	8.216E-010
1100.000	69.004	27.441	38.819	1.935E-008
1200.000	68.875	27.328	36.080	2.681E-007
1300.000	68.698	27.187	33.354	2.467E-006
1400.000	68.475	27.022	30.644	1.644E-005
1500.000	68.199	26.832	27.951	8.457E-005
1600.000	67.866	26.617	25.278	3.523E-004
1700.000	79.067	33.406	22.278	1.367E-003
1800.000	78.779	33.241	18.945	5.007E-003
1900.000	78.407	33.040	15.631	1.592E-002
2000.000	77.952	32.807	12.338	4.484E-002
2100.000	77.415	32.545	9.070	1.138E-001
2200.000	76.795	32.257	5.830	2.635E-001
2300.000	92.872	39.402	2.247	6.116E-001
2400.000	92.170	39.103	-1.678	1.422E+000
2500.000	91.363	38.774	-5.572	3.070E+000

Table 2. Thermodynamics of $2FeO + ZnO + H2O(g) = Fe_2ZnO_4 + H_2(g)$

| T	deltaH	deltaS	deltaG	K
K	kcal	cal/K	kcal	
300.000	-10.687	-15.496	-6.039	2.509E+004
400.000	-10.685	-15.493	-4.487	2.831E+002
500.000	-10.622	-15.355	-2.944	1.937E+001
600.000	-10.524	-15.178	-1.418	3.284E+000
700.000	-10.401	-14.988	0.091	9.368E-001
800.000	-10.253	-14.791	1.580	3.701E-001
900.000	-10.077	-14.584	3.049	1.818E-001
1000.000	-9.875	-14.371	4.496	1.040E-001
1100.000	-9.645	-14.152	5.923	6.655E-002
1200.000	-9.385	-13.926	7.327	4.629E-002
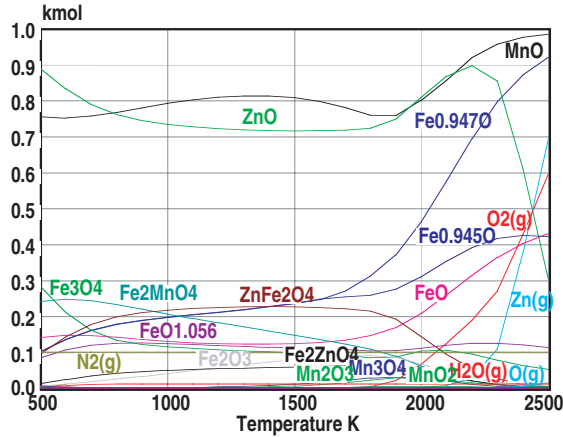
Fig. 1. Equilibrium amount (moles) from 1 mole of Fe2MnO4 and 1 mole of ZnO at 1 bar pressure as a function of temperature calculated with HSC (Ref. [2]). This composition was iteratively determined by reducing and removing the oxygen at 2100 K and hydrolysis with 1 mole of H2O(g) at 600 K. Under these conditions approximately 0.25 moles of hydrogen and 0.125 moles of oxygen are produced.
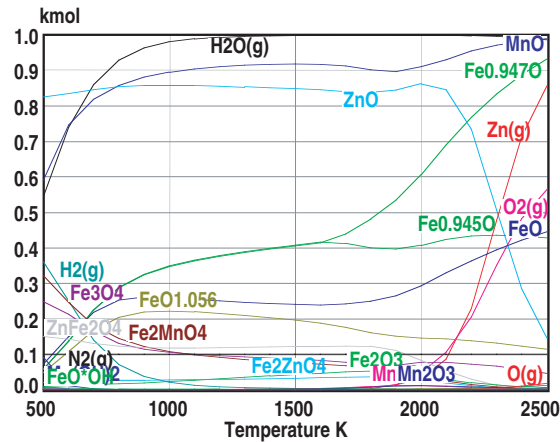
Fig. 2. Equilibrium amount (moles) from 1 mole of Fe2MnO4 and 1 mole of ZnO at 1 bar pressure as a function of temperature calculated with HSC (Ref. [2]). This composition was iteratively developed by reducing and removing the oxygen at 2100K and hydrolysis with 1 mole of H2O(g) at 600K.

Even if reasonable oxygen partial pressures can be attained at reasonable temperatures (<1800K) the analyses by Nakamura, Ref. [7], and Steinfeld, *et al.*, Ref. [8], suggest that unless sensible heat recovery approaches can be developed, the overall cycle thermal efficiency will be low.

To address sensible heat recovery in the Ferrite cycles, Sandia has invented a number of receiver/reactor configurations that utilize solid-to-solid thermal recuperation. An analysis was performed on the potential for achieving high conversion of solar input to higher heating value in hydrogen with these new concepts. The analysis is based on 36 kW net thermal input to the reactor and a reactor temperature in the range 1900K to 2100K and a pressure of 0.2 atm. The reactor design parameters are believed to be realistic of what might be achieved. Based on recent results by Kodama, Refs. [8,9], the ferrite is assumed to be impregnated on an inert carrier, zirconia, with 75% inert by weight. For the conditions modeled the amount of net hydrogen produced at 1900 to 2100 K is comparable to what Kodama reported at 1673K [9]. However,

because Kodama maintained a steady inert (nitrogen) gas flow during the thermal reduction, he shifted the equilibrium towards dissociation and his results are not directly comparable.

The thermodynamic analysis presented and discussed in the PID 2 analysis documentation indicates that reasonable efficiencies might be possible. Although, a similar analysis has not been done for the zinc manganese ferrite, similar results would be expected. Issues with the generation of a volatile zinc metal are a specific concern relative to PIDs 194 and 152. Otherwise, PID 2, 7, 194 are closely related.

These cycles have unique advantages of simplicity, direct heating of solids, inherent separation of the product oxygen and hydrogen, and avoid the use of corrosive chemicals. If either the thermodynamics can be shown to improve as a result of mixing metal oxides, ways to work at low hydrogen and oxygen generation pressures, or materials issues associated with very high temperatures (>2000 K) can be solved, then this class of thermodynamic cycles is very promising.

Table 3. Reduction/hydrolysis products calculated from HSC.

Hydrolyser Compound	600K Moles	Reduction Compound	2100 K Moles
H2O(g)	0.739	MnO	0.857
MnO	0.746	Fe0.947O	0.577
Fe0.947O	0.136	ZnO	0.867
ZnO	0.833	Zn(g)	0.007
Zn(g)	0.000	O2(g)	0.126
O2(g)	0.000	FeO	0.260
FeO	0.149	Fe0.945O	0.353
Fe0.945O	0.137	Fe3O4	0.106
H2(g)	0.249	Fe2MnO4	0.038
Fe2MnO4	0.244	ZnFe2O4	0.094
Fe3O4	0.211	FeO1.056	0.120
FeO1.056	0.107	N2(g)	0.100
ZnFe2O4	0.142	Fe2O3	0.046
N2(g)	0.100	Fe2ZnO4	0.032
Mn(OH)2	0.010	Mn3O4	0.019
Fe2O3	0.011	Mn2O3	0.022
Fe2ZnO4	0.024	O(g)	0.000
O(g)	0.000	H2O(g)	0.012
Mn3O4	0.000	H2(g)	0.000
Mn2O3	0.000	Zn0.5Fe2.5O4	0.000
FeO*OH	0.004	MnO2	0.004
Zn0.5Fe2.5O4	0.001	Mn(OH)2	0.000
H(g)	0.000	Zn0.7Fe2.3O4	0.000
Zn0.7Fe2.3O4	0.001	FeO*OH	0.000
MnO2	0.000	Zn0.1Fe2.9O4	0.000
Fe(OH)2	0.000	Zn0.3Fe2.7O4	0.000
Zn0.3Fe2.7O4	0.000	H(g)	0.000
Zn0.1Fe2.9O4	0.000	MnO*OH	0.000
Zn(OH)2	0.000	Fe(OH)2	0.000
OH(g)	0.000	OH(g)	0.000
MnO*OH	0.000	Zn(OH)2	0.000
Fe(OH)3	0.000	ZnMn2O4	0.000
ZnMn2O4	0.000	Fe(OH)3	0.000
Fe2O3*H2O	0.000	Fe2O3*H2O	0.000
Fe	0.000	Fe	0.000
Mn	0.000	Mn	0.000
Zn	0.000	Zn	0.000

REFERENCES

[1] UNLV Solar Thermal Hydrogen Generation Project, Department of Energy, 2004.

[2]   Computer program, "Outokumpu HSC Chemistry for Windows," Version 5.1 (HSC 5), Antti Roine, 02103-ORC-T, Pori, Finland, 2002.

[3]   Kaneko, H., Kojima, N., Hasegawa, N., Inoue, M., Uehara, R., Gokon, N., Tamura, Y., and T. Sano, "Reaction mechanism of H2 generation for H2O/Zn/Fe3O4 system," *Int. J. of Hydrogen Energy* Vol 27, pp. 1023-1028, 2002.

[4]   Tamaura, Y., Kojima, N., Hasegawa, N., Inoue, M., Uehara, R., Gokon, N, and H. Kaneko, "Stoichiometry studies of H2 generation reaction for H2O/Zn/Fe3O4 system, "*Int. J. of Hydrogen Energy* Vol 26, pp. 917-922, 2001.

[5]   Kaneko, H., Kodama, T., Gokon, N., Tamaura, Y., Lovegrove, K., and A. Luzzi, "Decomposition of Zn-ferrite for O2 generation by concentrated solar energy," Solar Energy Vol 76, pp. 317-322, 2004.

[6]   Inoue, M., Hasegawa, N., Uehara, R., Gokon, N., Kaneko, H., and Y. Tamaura, "Solar hydrogen generation with H2O/ZnO/MnFe2O4 system, *Solar Energy* Vol. 76 pp. 309-315, 2004.

[7]   Nakamura, T., "Hydrogen Production from Water Utilizing Solar Heat at High Temperatures," *Solar Energy*, Vol. 19, 467-475.

[8]   Steinfeld, A., Sanders, S., and R. Palumbo, "Design Aspects of Solar Thermochemical Engineering –A Case Study: Two-Step Water-Splitting Cycle Using the Fe3O4/FeO Redox System," *Solar Energy* Vol. 65, No. 1, pp43-53, 1999.

PID 196 – OR 582 ASSESSMENT, REV. 1

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Temp. (°C)
CO2-15	$3CO_2 + 6NaI(aq) + 6NH_3 + 3H_2O =$ $3Na_2CO_3(aq) + 6NH_4I(aq)$	0.33	100
NH4I	$2NH_4I(g) = I_2(g) + 2NH_3 + H_2(g)$	1	370
I2-25	$3I_2(s) + 6Na_2CO_3(aq) + 3H_2O =$ $6NaHCO_3(aq) + 5NaI(aq) + NaIO_3$	0.33	80
NaHCO3-1	$6NaHCO_3(s) = 3CO_2 + 3Na_2CO_3(s) +$ $3H_2O$	0.33	127
NaIO3	$2NaIO_3(s) = 2NaI(s) + 3O_2$	0.33	430

CONCLUSIONS

Two steps of this cycle will not proceed as written. Attempts to modify the cycle to make it feasible were unsuccessful. The cycle is assigned an efficiency of zero.

DISCUSSION

REACTION NH4I-1

HI is the thermodynamically favored reaction product of the NH4I-1 reaction therefore this cycle is not feasible as proposed. This reaction might be replaced by two reactions in sequence:

$$NH_4I = NH_3(g) + HI(g)$$

$$2HI(g) = H_2(g) + I_2(g)$$
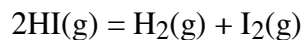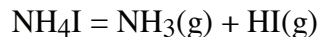
but there does not seem to be any practical way of separating the $NH_3(g)$ and $HI(g)$. If they are cooled, the NH4I will reform and if one tries to carry the NH_3 along with the HI through the catalytic HI decomposition step, the NH_3 will likely decompose as NH_3 is thermodynamically unstable above 180°C at atmospheric pressure and even at 10,000 bar, 370°C, as much hydrogen is present from NH_3 decomposition as from HI decomposition. Without a means of separating NH_3 and HI at temperature the cycle is not feasible.

Even if a separation for NH3 and HI existed, the cycle would still have major problems.

REACTION CO2-15

The reaction CO2-15 does not proceed as indicated, it produces bicarbonate instead of carbonate. The bicarbonate is less soluble than iodide, but the cations partition between the solid and soluble phases. In aqueous solution, with excess CO_2, HSC-5 indicates:

Figure 1 shows the effect of pressure on Reaction CO2-15 when run under optimal conditions. The temperature is $80°C$, not the proposed $100°C$ and additional CO2 and water are added to drive the reaction towards the products and separate the products from each other. The reaction products are more easily separated than indicated on the website as the iodide salts are soluble and the carbonates are relatively insoluble. Note though that the carbonates primarily occur as the bicarbonate. Reaction NaHCO3-1, which originally recycled the byproduct of reaction I2-25 now becomes part of the mainline process. It also handles the mixed solid carbonates that accompany the NaHCO3. The mixed carbonates include small to moderate amounts of Na2CO3, Na2CO3*10H2O, Na2CO3*3NaHCO3, Na2CO3*7H2O, Na2CO3*H2O, and Na2CO3*NaHCO3*2H2O.
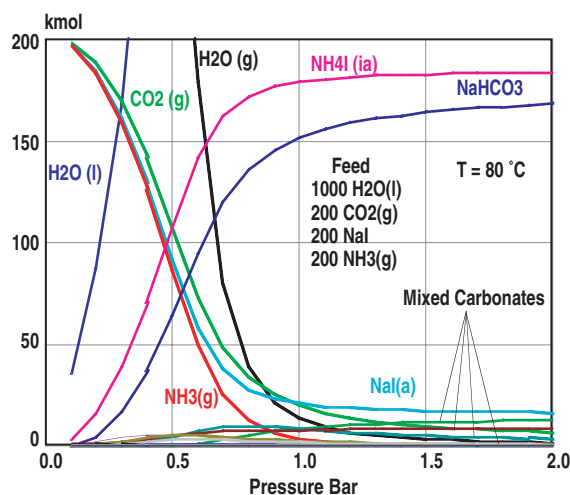

Fig. 1.   Affect of pressure on reaction CO2-15.

The dissolved NH4I product, which must be recovered from the aqueous phase by evaporation of the water, contains a small amount of NaI.

REACTION NaHCO3-1

Processing the NaHCO3 and mixed carbonates from reaction CO2-15 is relatively straightforward, although as indicated in Fig. 2, a temperature of over $250°C$ is required.

REACTION I2-25

Figure 3 shows that the carbonate and iodated products of Reaction I2-25 can be separated by solubility, but the result is the opposite of that indicated in the proposed reaction scheme. The iodate is soluble, given enough water, and the carbonate is insoluble. Unfortunately the bicarbonate is also soluble, as us the iodide and the amount of water required to solublize the iodate is extremely large.
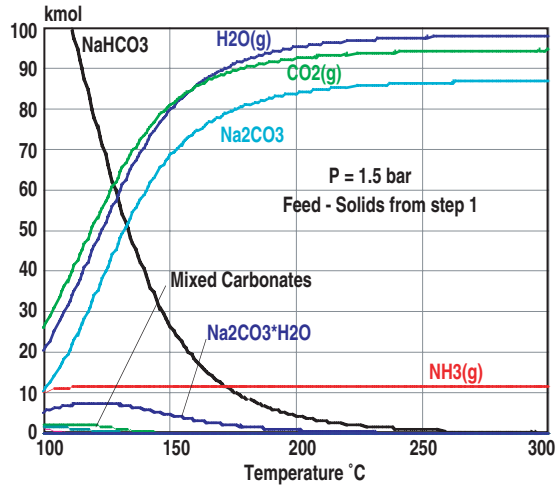
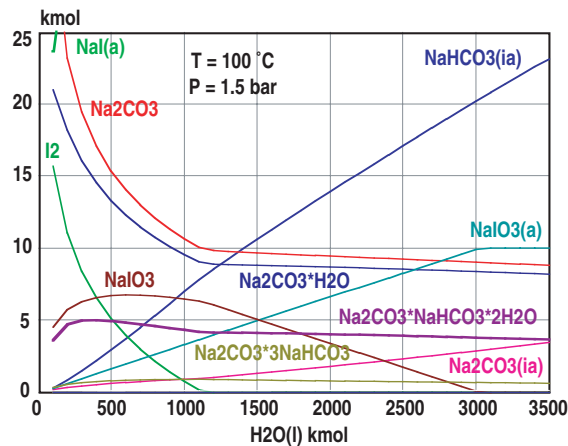Fig. 2.   Affect of temperature on reaction NaHCO3-1.

Fig. 3.   Affect of temperature on reaction I2-25.

At this point it is obvious that the cycle will have a negligible efficiency. Only 1/3 of the projected amount of NaIO3 is available for processing in Reaction NaIO3-1. For each mole of NaICO3 processed, 300 moles of water must be evaporated. Each mole of NaIO3 is accompanied through the oxygen generation step by 2 moles of NaHCO3, 1 mole of Na2CO3 and 5 moles of NaI.

REACTION NaIO3-1

The Na2CO3 and NaI that accompany the NaIO3 have no effect except for the additional heat needed to raise their temperature to the 550°C required for the decomposition of NaIO3. The NaHCO3 accompanying theNaIO3 decomposes into Na2CO3, CO2 and H2O. The CO2 must be scrubbed from the O2 to recover the CO2.

SUMMARY

Inserting the correct reactions, phases and multipliers for the required conditions explained below results in the following table:

Reaction Code	Formula	Multiplier	Temp. (ºC)
CO2-15	$CO_2(g) + NaI(a) + NH_3(a) + H_2O(l) = NaHCO_3(s) + NH_4I(a)$	2	80
NEW	$NH_4I(g) = HI(g) + NH_3(g)$	2	600
HI-1	$2HI(g) = I_2(g) + H_2(g)$	1	300
I2-25	$3I_2(a) + 6Na_2CO_3 + 3H_2O(l) = 6NaHCO_3 + 5NaI(a) + NaIO_3$	0.33	100
NaHCO3-1	$2NaHCO_3(s) = CO_2(g) + Na_2CO_3(s) + H_2O(g)$	1	300
NaIO3	$2NaIO_3(s) = 2NaI(s) + 3O_2(g)$	0.167	550

The five reactions initially in the cycle have increases to six. There is a major cross contamination between the products of the low temperature aqueous reaction, the amount of recycle has increased dramatically and there remains the problem of an infeasible high temperature gas-gas separation. No further work on this cycle appears to be justified.

PID 198 – CALCIUM BROMIDE

Reaction Code	Formula	Multiplier	Temp. (ºC)
CaBr2-3	CaBr2(s) + H2O(g) = CaO(s) + 2 HBr(g)	1.00	727
Br2	2Br2(g) + 2CaO(s) = 2CaBr2(s) + O2	0.50	600
HBr-5	2 HBr(g) + plasma = Br2(g) + H2	1.00	25

SUMMARY

The efficiency of this cycle is probably very low, near zero, due to the

CaBr2-3 REACTION

$\Delta G > 0$ for this reaction at all temps less than 2500°C. This step will be very inefficient with a flowing inert gas stream requiring separation of H2O and HBr from the inert gas.

Br2 REACTION

This reaction is spontaneous at the temperature proposed.

HBr-5 REACTION

The decomposition of HBr to elements is thermodynamically "uphill" at all temperatures. Not only will the use of a plasma discharge probably be energy inefficient, but recombination of H2 + Br2 to make HBr upon cooldown will pose a serious separation problem to solve. So we anticipate the mass efficiency to be low, as well as a low energy efficiency.

PID 199-IRON CHLORIDE-11

Iron-Chloride-6 was called Mark 14 by its proponents.

Reaction Code	Formula	Multiplier	Temp (°C)
FeCl2-5	3 FeCl2(l) + 4H2O = Fe3O4 + 6HCl(g) + H2	1	650
Fe3O4-13	6 Fe3O4 + 3 Cl2 = 8 Fe2O3 + 2 FeCl3	0.167	230
Fe2O3-1	Fe2O3 + 6 HCl = 2 FeCl3 + 3 H2O	1.33	230
Cl2-1	2 Cl2(g) + 2H2O(g) = 4HCl(g) + O2(g)	0.5	800
FeCl3-1	2 FeCl3 = Cl2(g) + 2FeCl2	1.5	350

SUMMARY

The ISPRA workers decided the thermal efficiency would be <20% and they abandoned work on this cycle.

FeCl2-5 REACTION

This reaction as written has a very positive G, 206.257 kJ per mole H2 formed, so the workers (1) required a flowing system of water over a bed to drive the reaction to the right.

Fe3O4-13, Fe2O3-1, and Cl2-1 REACTIONS

These reactions proceeded with little problem.

FeCl3-1 REACTION

The equilibrium for this reaction lies to the left, so they required considerable recycle. This step set a serious limit on the thermal efficiency of the cycle.

The proponents felt that Mark 15 (PID 200) was an improvement over Mark 14 (PID 199, this cycle), and estimated the Mark 15 efficiency at 20%, and abandoned all Fe-Cl thermochemical cycles.

REFERENCES

1.   G.E. Beghi, "A Decade of Research on Thermochemical Hydrogen at the Joint Research Centre, ISPRA", Int. J. Hydrogen Energy, 11(12), 761, 1986.

PID 200-IRON CHLORIDE-12

Iron Chloride-7 was called Mark 15 by its proponents.

Reaction Code	Formula	Multiplier	Temp (°C)
FeCl2-5	3FeCl2(l) + 8H2O = Fe3O4(s) + 6 HCl + H2	1	650
Fe3O4-5	Fe3O4 + 8HCl = FeCl2 + 2FeCl3 + 4H2O	1	230
Cl2-1	2Cl2(g) + 2H2O(g) = 4HCl(g) + O2(g)	0.5	800
FeCl3-1	2FeCl3 = Cl2(g) + 2FeCl2	1	350

SUMMARY

The ISPRA workers decided the thermal efficiency would be 20% and they abandoned work on this and all earlier cycles.

FeCl2-5 REACTION

This reaction as written has a very positive G, 206.257 kJ per mole H2 formed, so the workers (1) required a flowing system of water over a bed to drive the reaction to the right.

Fe3O4-5 and Cl2-1 REACTIONS

These reactions proceeded with little problem.

FeCl3-1 REACTION

The equilibrium for this reaction lies to the left, so they required considerable recycle. This step set a serious limit on the thermal efficiency of the cycle.

The proponents felt that Mark 15 (PID 200) was an improvement over all previous Mark cycles they had developed, estimated the Mark 15 efficiency at 20%, and abandoned all Fe-Cl thermochemical cycles.

REFERENCES

1. G.E. Beghi, "A Decade of Research on Thermochemical Hydrogen at the Joint Research Centre, ISPRA", Int. J. Hydrogen Energy, 11(12), 761, 1986.

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PID 201– Carbon Oxides

This process is based on the following chemical reactions in the UNLV database:

Reaction Code	Formula	Multiplier	Max. Temp. (ºC)
CO2-1	2CO2 = 2CO + O2	0.5	2200
CO-6	CO + H2O = CO2 + H2	1	150

CO2-1 has 12% conversion at 2200°C. With an excess of 13.1 mol CO2, this reaction can be shifted to approximate the completion of CO2-1.

Per the attached flowsheet, the solar heat load is 607 MJ and the electric load is 78 MJ, which includes 71 MJ for the cooling requirement for cryogenic separation of the CO2 stream.

A membrane separation is recommended for the O2-CO separation and a PSA unit for the H2 recovery.

The overall efficiency of this process is 37%.

PID 202 – METHANOL-FORMALDEHYDE

This process is based on the following chemical reactions:

Reaction codes	Formula	Multiplier	Temp(°C)
CH4	CH4(g) + H2O(g) = CO(g) + H2(g)	1.00	850
CO-1	CO(g) + 2 H2(g) = CH3OH	1.00	250
CH3OH-3	CH3OH = CH2O(g) + H2(g)	1.00	650
CH2OH	2CH2O(g) + 2H2 = 2 CH4 + O2	0.50	100

SUMMARY

The efficiency of this cycle is zero.

DISCUSSION

CH2OH REACTION

ΔG for this reaction is very positive at all temperatures. In effect, one is saying that methane and oxygen do not burn (the reverse reaction) at 100°C, or above some higher temperature. One also risks mixing H_2 and O_2 in the reaction, which is another explosive mixture. The mass efficiency of this step is zero.

CO-1 REACTION

$CO + H_2$ may form methanol below about 135°C (where $\Delta G = 0$ at standard states), and one may have a small amount of methanol formed at 250°C.

CH3OH-3 REACTION

This reaction is spontaneous above about 520°C.

CH4 REACTION

This reaction is commercially known, above about 600°C.