GA–A23451

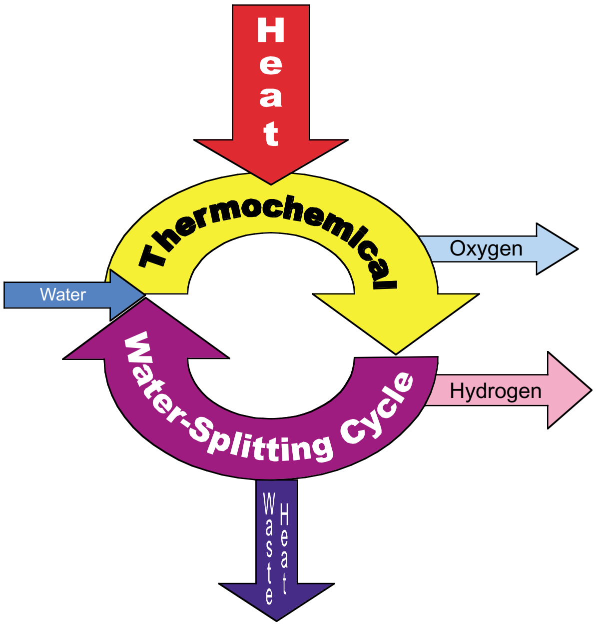
HIGH EFFICIENCY GENERATION OF HYDROGEN FUELS USING NUCLEAR POWER

ANNUAL REPORT TO THE U.S. DEPARTMENT OF ENERGY

AUGUST 1, 1999 THROUGH JULY 31, 2000

by
L.C. BROWN, J.F. FUNK, and S.K. SHOWALTER

Prepared under
Nuclear Energy Research Initiative (NERI)
Grant No. DE-FG03-99SF21888
for the U.S. Department of Energy



DATE PUBLISHED: JULY 2000

DISCLAIMER

GA–A23451

HIGH EFFICIENCY GENERATION OF HYDROGEN FUELS USING NUCLEAR POWER

ANNUAL REPORT TO THE U.S. DEPARTMENT OF ENERGY

AUGUST 1, 1999 THROUGH JULY 31, 2000

by
L.C. BROWN, J.F. FUNK,* and S.K. SHOWALTER†

*University of Kentucky, Lexington, Kentucky.
†Sandia National Laboratories, Albuquerque, New Mexico.

Prepared under
Nuclear Energy Research Initiative (NERI)
Grant No. DE-FG03-99SF21888
for the U.S. Department of Energy

GENERAL ATOMICS PROJECT 30047
DATE PUBLISHED: JULY 2000

EXECUTIVE SUMMARY

Currently no large scale, cost-effective, environmentally attractive hydrogen production process is available for commercialization nor has such a process been identified. Hydrogen is a promising energy carrier, which potentially could replace the fossil fuels used in the transportation sector of our economy. Fossil fuels are polluting and carbon dioxide emissions from their combustion are thought to be responsible for global warming.

The purpose of this work is to determine the potential for efficient, cost-effective, large-scale production of hydrogen utilizing high temperature heat from an advanced nuclear power station. The benefits of this work will include generation of a low-polluting transportable energy feedstock in a highly efficient method that has little or no implication for greenhouse gas emissions from an energy source whose availability and sources are domestically controlled. This will help to ensure energy surety to a future transportation/energy infrastructure that is not influenced/controlled by foreign governments.

This report describes work accomplished during the first year (Phase 1) of a three year project whose objective is to "define an economically feasible concept for production of hydrogen, by nuclear means, using an advanced high temperature nuclear reactor as the energy source." The emphasis of the first phase was to evaluate thermochemical processes which offer the potential for efficient, cost-effective, large-scale production of hydrogen from water, in which the primary energy input is high temperature heat from an advanced nuclear reactor and to select one (or, at most three) for further detailed consideration.

The main elements comprising Phase 1 are:

- A detailed literature search to develop a database of all published thermochemical cycles.
- Develop a rough screening criteria to rate each cycle.
- Perform a first round of screening reducing initial list to 20–30 cycles.
- Report on the results of the first round.
- Perform a second round of screening using refined criteria and reducing the number of cycles under consideration to 3 or less.
- Report on the results of Phase 1.

Ten databases were searched (e.g., Chemical Abstracts, NTIS, etc.), and over 800 literature references were located which pertain to thermochemical production of hydrogen from water. The references were organized in a computerized literature database. Over 100 thermochemical water-splitting cycles were identified. The cycle data was also organized into a computer searchable database.

The first round of screening, using defined screening criteria and quantifiable metrics, yielded 25 cycles for more detailed study. The second round of screening, using refined criteria reduced the 25 to 2.

The two cycles selected for final consideration are the UT-3 cycle and the sulfur-iodine cycle. The UT-3 cycle was invented at the University of Tokyo and much of the early development was done there. This cycle has been studied extensively in Japan by a number of organizations, including Toyo Engineering and Japan Atomic Energy Research Institute (JAERI). After considering several different flowsheets making use of the UT-3 cycle, JAERI selected the so-called Adiabatic UT-3 process for further development. The predicted efficiency of the Adiabatic UT-3 process varies between 35% and 50% depending upon the efficiency of membrane separators, which are under development, and whether electricity is co-generated along with the hydrogen. A 10% overall efficiency increase is projected if co-generation is employed. Much of the type of work we contemplated, such as pilot plant operation, materials studies, and flow sheet development has already been performed for this cycle in Japan.

The sulfur-iodine cycle remains the cycle with the highest reported efficiency, based on an integrated flowsheet. Various researchers have pointed out improvements that should increase the already high efficiency (52%) of this cycle and, in addition, lower the capital cost. In Phases 2 and 3 we will investigate the improvements that have been proposed to the sulfur-iodine cycle and will generate an integrated flowsheet describing a thermochemical hydrogen production plant powered by a high-temperature nuclear reactor. The detailed flowsheet will allow us to size the process equipment and calculate the hydrogen production efficiency. We will finish by calculating the capital cost of the equipment and estimate the cost of the hydrogen produced as a function of nuclear power costs.

It would be advantageous, but not essential, if some form of joint collaboration can be established with the Japanese. In particular, we would like access to their latest experimental results on the chemistry of the sulfur-iodine cycle. Although we will concentrate our effort on the sulfur-iodine cycle, we retain an interest in the UT-3 cycle. The work we have proposed, and which we will carry out for the sulfur-iodine cycle has, to a large part, already been performed in Japan for the Adiabatic UT-3 process. We would encourage the Japanese to perform the required non-steady-state analysis of the

Adiabatic UT-3 process. After the Japanese and we have completed our respective tasks, we will have two processes from which to select a means of producing hydrogen using nuclear power.

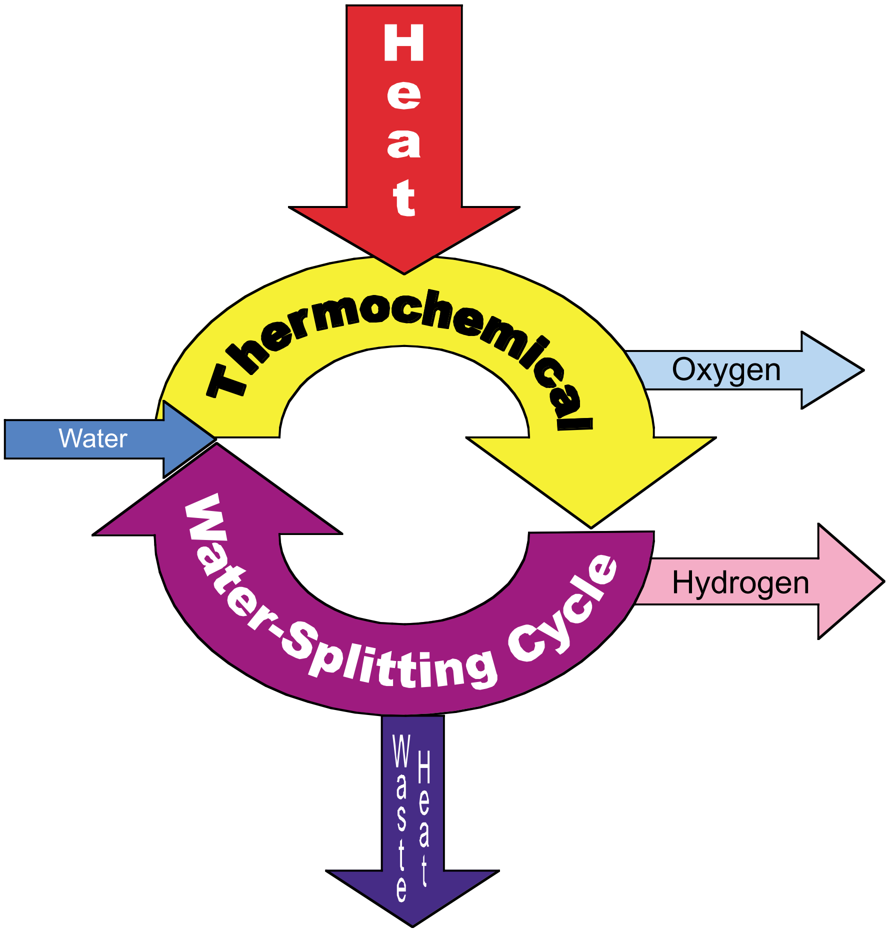


TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

Combustion of fossil fuels, used to power transportation, generate electricity, heat homes, and fuel industry, provides 86% of the world's energy [1, 2]. Drawbacks to fossil fuel utilization include limited supply, pollution, and carbon dioxide emissions. Carbon dioxide emissions, thought to be responsible for global warming, are now the subject of international treaties [3, 4]. Together, these drawbacks argue for the replacement of fossil fuels with a less-polluting potentially renewable primary energy such as nuclear energy. Conventional nuclear plants readily generate electric power but fossil fuels are firmly entrenched in the transportation sector. Hydrogen is an environmentally attractive transportation fuel that has the potential to displace fossil fuels. Hydrogen will be particularly advantageous when coupled with fuel cells. Fuel cells have higher efficiency than conventional battery/internal combustion engine combinations and do not produce nitrogen oxides during low-temperature operation. Contemporary hydrogen production is primarily based on fossil fuels and most specifically on natural gas. When hydrogen is produced using energy derived from fossil fuels, there is little or no environmental advantage.

There is currently no large scale, cost-effective, environmentally attractive hydrogen production process, available for commercialization, nor has such a process been identified. The objective of this work is to find an economically feasible process for the production of hydrogen, by nuclear means, using an advanced high-temperature nuclear reactor as the primary energy source. Hydrogen production by thermochemical water-splitting, a chemical process that accomplishes the decomposition of water into hydrogen and oxygen using only heat or, in the case of a hybrid thermochemical process, by a combination of heat and electrolysis, could meet these goals.

Hydrogen produced from fossil fuels has trace contaminants (primarily carbon monoxide) that are detrimental to precious metal fuel cells, as is now recognized by many of the world's largest automobile companies. Thermochemical hydrogen will not contain carbon monoxide as an impurity at any level. Electrolysis, the alternative process for producing hydrogen using nuclear energy, suffers from thermodynamic inefficiencies in both the production of electricity and in electrolytic parts of the process. The efficiency of electrolysis (electricity to hydrogen) is currently about 80%. Electric power generation efficiency would have to exceed 65% (thermal to electrical) for the combined efficiency to exceed the 52% (thermal to hydrogen) calculated for one thermochemical cycle.

Thermochemical water-splitting cycles have been studied, at various levels of effort, for the past 35 years. They were extensively studied in the late 70s and early 80s but received little attention in the past 10 years, particularly in the U.S. While there is no question about the technical feasibility and the potential for high efficiency, cycles with proven low cost and high efficiency have yet to be developed commercially. Over one hundred cycles have been proposed, but substantial research has been executed on only a few.

This report describes work accomplished during the first year (Phase 1) of a three-year project whose objective is to "define an economically feasible concept for production of hydrogen, by nuclear means, using an advanced high temperature nuclear reactor as the energy source." The emphasis of the first phase was to evaluate thermochemical processes which offer the potential for efficient, cost-effective, large-scale production of hydrogen from water in which the primary energy input is high temperature heat from an advanced nuclear reactor and to select one (or, at most three) for further detailed consideration.

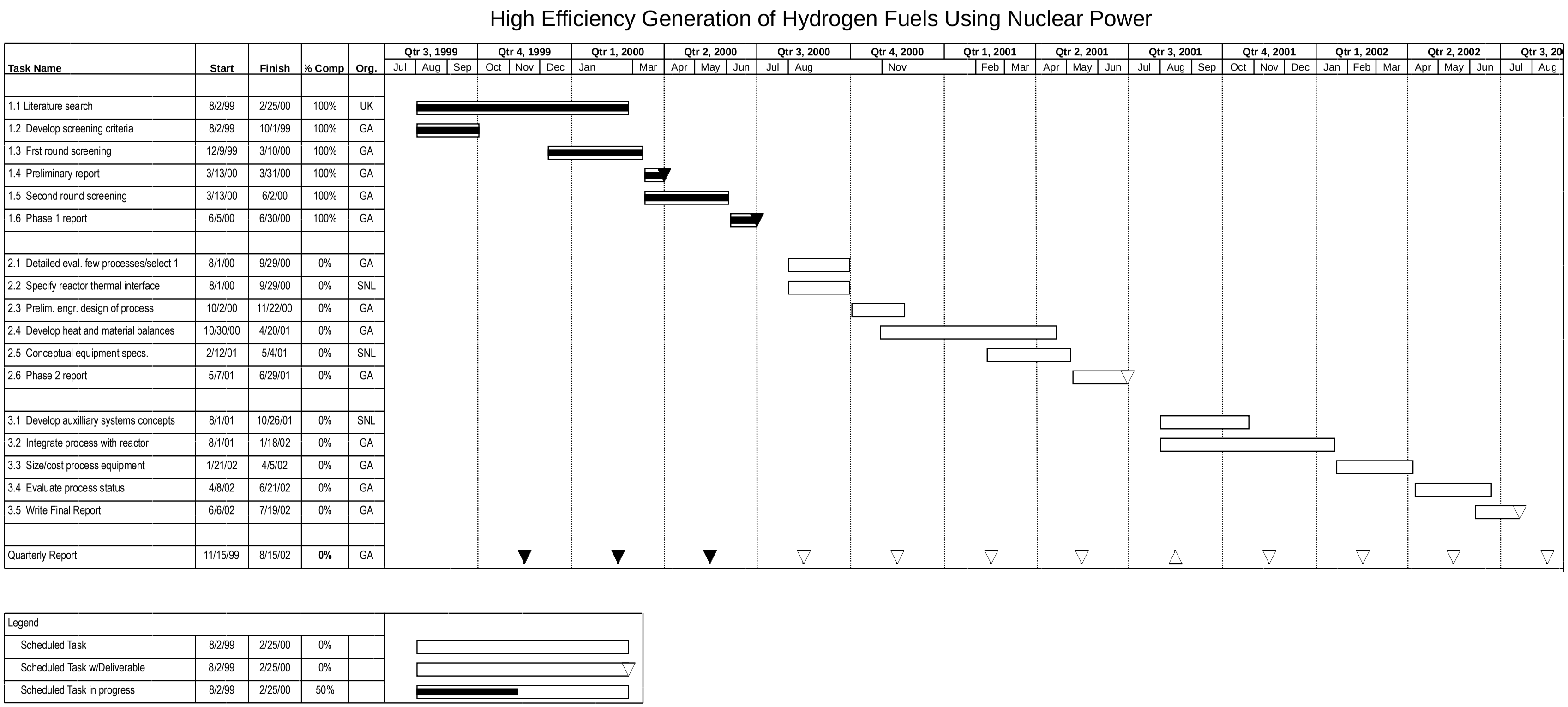
This work is performed as a collaborative effort between General Atomics (GA), the University of Kentucky (UK) and Sandia National Laboratories (SNL) under the Department of Energy under Nuclear Energy Research Initiative (NERI) Grant No. (DE-FG03-99SF21888 (GA/UK).

The work was divided into several tasks. Each task was performed according to the predetermined schedule (Fig. 1) and all technical tasks were completed as scheduled. All of the collaborators were involved in every task but one organization had responsibility for the task. The Phase 1 tasks and the responsible organizations are:

Literature survey of new processes	UK
– Cycle database	SNL
Develop screening criteria	GA
Carry out first round screening	GA
Short report on conclusions	GA
Carry out second round screening	GA
Write Phase 1 report	GA

As reported here, an exhaustive literature search was performed to locate all cycles previously proposed. The cycles located have been screened using objective criteria, to determine which can benefit, in terms of efficiency and cost, from the high-temperature capabilities of advanced nuclear reactors. The literature search, the development of the screening criteria, the screening process and the results will be described in the following sections. Subsequently, the cycles were analyzed as to their adaptability to advanced high-temperature nuclear reactors, considering among other things, the latest improvements in materials of construction and new membrane separation technologies. Guided by the results of the secondary screening process, one cycle was selected for integration into the advanced nuclear reactor system.

In Phases 2 and 3, which are to follow, the required flowsheets will be developed and preliminary engineering estimates of size and cost will be made for major pieces of equipment. From this information, a preliminary estimate of efficiency and cost of hydrogen will be made. This follow-on effort will perform the work scope and follow the schedule of the original proposal, as amended prior to contract award.



High Efficiency Generation of Hydrogen Fuels Using Nuclear Power

Task Name	Start	Finish	% Comp	Org.
1.1 Literature search	8/2/99	2/25/00	100%	UK
1.2 Develop screening criteria	8/2/99	10/1/99	100%	GA
1.3 First round screening	12/9/99	3/10/00	100%	GA
1.4 Preliminary report	3/13/00	3/31/00	100%	GA
1.5 Second round screening	3/13/00	6/2/00	100%	GA
1.6 Phase 1 report	6/5/00	6/30/00	100%	GA
2.1 Detailed eval. few processes/select 1	8/1/00	9/29/00	0%	GA
2.2 Specify reactor thermal interface	8/1/00	9/29/00	0%	SNL
2.3 Prelim. engr. design of process	10/2/00	11/22/00	0%	GA
2.4 Develop heat and material balances	10/30/00	4/20/01	0%	GA
2.5 Conceptual equipment specs.	2/12/01	5/4/01	0%	SNL
2.6 Phase 2 report	5/7/01	6/29/01	0%	GA
3.1 Develop auxilliary systems concepts	8/1/01	10/26/01	0%	SNL
3.2 Integrate process with reactor	8/1/01	1/18/02	0%	GA
3.3 Size/cost process equipment	1/21/02	4/5/02	0%	GA
3.4 Evaluate process status	4/8/02	6/21/02	0%	GA
3.5 Write Final Report	6/6/02	7/19/02	0%	GA
Quarterly Report	11/15/99	8/15/02	**0%**	GA

Legend				
Scheduled Task	8/2/99	2/25/00	0%	
Scheduled Task w/Deliverable	8/2/99	2/25/00	0%	
Scheduled Task in progress	8/2/99	2/25/00	50%	

Fig. 1. Schedule of all three phases.

2. THERMOCHEMICAL WATER SPLITTING

Thermochemical water-splitting is the conversion of water into hydrogen and oxygen by a series of thermally driven chemical reactions. The direct thermolysis of water requires temperatures in excess of 2500°C for significant hydrogen generation.

(1*) $H_2O \rightarrow H_2 + {}^1/_2O_2$ (2500°C min)

At this temperature, 10% of the water is decomposed and 90% of the water would be recycled. In addition, a means of preventing the hydrogen and oxygen from recombining upon cooling must be provided or no net production would result. A thermochemical water-splitting cycle accomplishes the same overall result using much lower temperatures. The sulfur-iodine cycle is a prime example of a thermochemical cycle. It consists of three chemical reactions, which sum to the dissociation of water.

(2) $H_2SO_4 \rightarrow SO_2 + H_2O + {}^1/_2O_2$ (850°C)

(3) $I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$ (120°C)

(4) $2HI \rightarrow I_2 + H_2$ (450°C)

(1) $H_2O \rightarrow H_2 + {}^1/_2O_2$

The thermochemical cycle has significant conversion at much lower temperatures. With a suitable catalyst, the high-temperature reaction (2) reaches 10% conversion at only 510°C, and 83% conversion at the indicated temperature of 850°C. Moreover, there is no need to perform a high temperature separation as the reaction ceases when the stream leaves the catalyst.

Energy, in the form of heat, is input to a thermochemical cycle via one or more endothermic high-temperature chemical reactions. Similar to the way that a heat engine must reject heat to a low temperature sink, a thermochemical cycle rejects heat via one or more exothermic low temperature chemical reactions. Finally, other thermally neutral chemical reaction may be required to complete the cycle so that all the reactants, other than water, are regenerated. In the case of the S-I, cycle most of the input heat goes into the oxygen generating reaction, the dissociation of sulfuric acid. Sulfuric acid and

---

*Note: Each chemical reaction retains a unique "reaction number" throughout this report.

hydrogen iodide are formed in the endothermic reaction of the S-I cycle and the hydrogen is generated in the mildly endothermic decomposition of hydrogen iodide.

The combination of high temperature endothermic reactions, low temperature exothermic reactions and energy neutral closing reactions are not sufficient for a cycle to be thermodynamically realizable. Each reaction must also have favorable ΔG (Gibbs free energy). The ΔG for a reaction is a measure of the concentrations of the reactants and products of the reaction at equilibrium. A reaction is favorable if ΔG is negative, or at least not too positive. A slightly positive ΔG does not mean that the reaction does not proceed, only that the reaction does not proceed far and high recycle may be required. It is possible to shift a reaction equilibrium by increasing the concentrations of the products or reducing the concentration of reactants. Each of the four chemical reactions of the UT-3 Cycle, in fact, has a slightly positive ΔG. The flow of gaseous reactant through the bed of solid reactants sweeps the gaseous products away resulting in total conversion of the solid reactants to solid products.

(5) $2Br_2(g) + 2CaO(s) \rightarrow 2CaBr_2(s) + {}^1/_2O_2(g)$ (672°C)

(6) $3FeBr_2(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 6HBr(g) + H_2(g)$ 560°C)

(7) $CaBr_2(s) + H_2O(g) \rightarrow CaO(s) + 2HBr(g)$ (760°C)

(8) $Fe_3O_4(s) + 8HBr(g) \rightarrow Br_2(g) + 3FeBr_2(s) + 4H_2O(g)$ (210°C)

(1) $H_2O(g) \rightarrow H_2(g) + {}^1/_2O_2(g)$

Sometimes it is even possible to electrochemically force a non-spontaneous reaction: such a process is termed a hybrid thermochemical cycle to distinguish it from a pure thermochemical cycle. Hybrid cycles are often considered along with pure thermochemical cycles and we do so here. The hybrid sulfur cycle, also known as the Westinghouse cycle or as the Ispra Mark 11 cycle has the same high temperature endothermic reaction as the sulfur-iodine cycle. The hybrid cycle is closed by the electrochemical oxidation of sulfur dioxide to sulfuric acid.

(2) $H_2SO_4 \rightarrow SO_2 + H_2O + {}^1/_2O_2$ (850°C)

(9) $SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2$ (80°C electrolysis)

(1) $H_2O \rightarrow H_2 + {}^1/_2O_2$

3. PROJECT DATABASES

An important part of the preliminary screening effort dealt with the details of organizing and presenting data in a easy to use form, i.e., the organization of project specific databases. There are many sources of compiled literature data. Each of these commercial databases uses its own method of organizing and presenting the same generic type of data. This makes it important that the data from the various sources be translated into a common format for comparison and duplicate removal. EndNote [5], a widely accepted and readily available database program designed to manage bibliographic information, is used to maintain the project literature database. EndNote provides the tools required for translating the output data from any of the various literature database search engines into a common format. Each EndNote entry includes the bibliographic entry, tracking information and, if available, an abstract.

A second database was required to keep track of all the thermochemical cycles. Here we had four main goals:

1. Inclusion of all the information required to screen the cycles
2. Ability to output reports with various parameters for the different cycles.
3. Ability to search for common threads among the various cycles and display the data electronically in alternative ways.
4. A means of preventing the same cycle from being entered multiple times.

Together, these indicated that we needed a relational database: we selected MS Access 2000 as the tool with which to organize the cycle data.

Figure 2 indicates the organization of the cycle database. A cycle represents a complete series of chemical reactions to produce water thermochemically (as in the University of Tokyo, UT-3 cycle). Reactions are the discreet reaction steps within a specific cycle. There are four main data table areas within the database: general, reactions, authors and references. Each of these tables was linked with a junction table that allowed a one-to-many relationship linked back to the general table. This allowed for a reference or reaction that was linked to multiple cycles to be represented only once in the database. The cycles were all uniquely identified by a primary identification (ID) number that was assigned automatically by the database in the order that they were entered. Some primary IDs are missing because, after entering cycles into the database and upon further examination, they were discovered to be duplicates of cycles already in

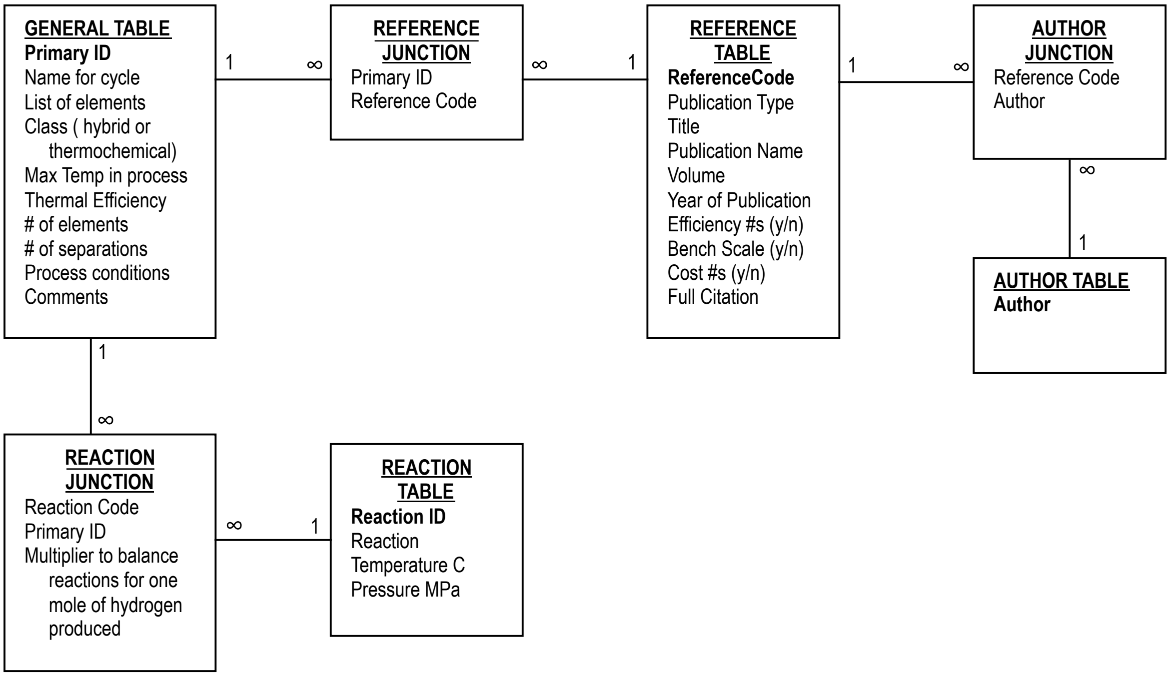
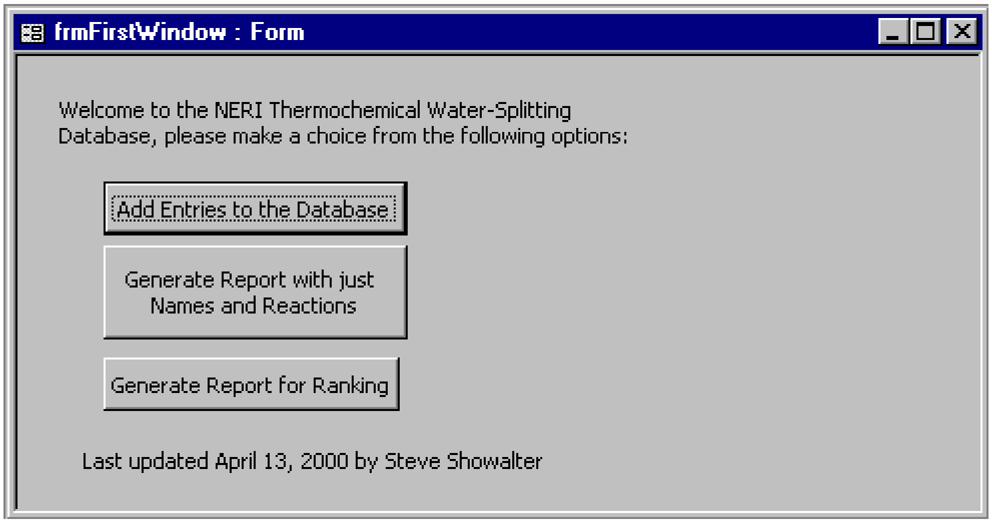


Fig. 2. Database structural relationship.

the database, or were not complete cycles. Names were assigned to ease reference in discussion when ranking the cycles. The names associated with the cycles were created from either given names in the references or names created from the compounds used in the cycle. The database format makes it easy to search for commonality between various cycles using a query (e.g. similar reactions, authors, compounds, etc.). The cycle database contains the details of the chemical reactions and process conditions for the process, as well as the abbreviated bibliographic information/literature references that describe or refer to the cycles. The start screen gives various choices to the researcher searching or entering data into the database (Fig. 3).

The first button takes you into the main database data entry area. The last two buttons generate reports for printing out lists of cycles and/or reactions. Pressing the first button takes you to the page represented by Fig. 4. The scroll bars and arrows at the bottom allow a user to “walk through” the database in sequential order. The raised buttons execute forms or queries to search or update the database.

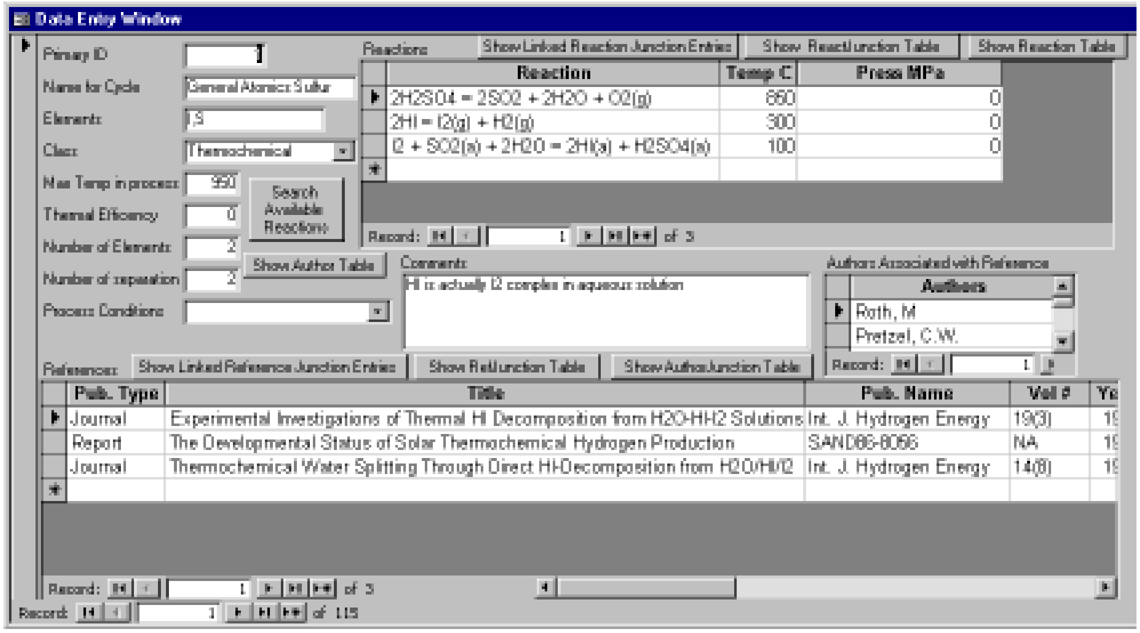
Each of the junction tables needs a unique identifier to the attached data table to link with the primary ID and general table entry of the cycle. Therefore, there were identifiers for each reference, reaction and author independent of the primary ID identifier. Reference IDs were based on the initials of the first author of the reference followed by a number if needed to uniquely identify the reference. If only a company or institution was identified as the author, the uppercase initials are used to identify the reference. This



Welcome to the NERI Thermochemical Water-Splitting Database, please make a choice from the following options:

Last updated April 13, 2000 by Steve Showalter

Fig. 3. Start page for thermochemical database.



Primary ID	1
Name for Cycle	General Atomics Sulfur
Elements	I,S
Class	Thermochemical
Max Temp in process	950
Thermal Efficiency	0
Number of Elements	2
Number of separation	2
Process Conditions	

Reactions

Reaction	Temp C	Press MPa
2H2SO4 = 2SO2 + 2H2O + O2(g)	860	0
2HI = I2(g) + H2(g)	300	0
I2 + SO2(a) + 2H2O = 2HI(a) + H2SO4(a)	100	0

Record: 1 of 3

Comments: HI is actually I2 complex in aqueous solution

Authors Associated with Reference

Authors
Roth, M
Pretzel, C.W.

Record: 1

References:

Pub. Type	Title	Pub. Name	Vol #	Ye
Journal	Experimental Investigations of Thermal HI Decomposition from H2O-HI-I2 Solutions	Int. J. Hydrogen Energy	19(3)	19
Report	The Developmental Status of Solar Thermochemical Hydrogen Production	SAND86-8066	NA	19
Journal	Thermochemical Water Splitting Through Direct HI-Decomposition from H2O/HI/I2	Int. J. Hydrogen Energy	14(8)	19

Record: 1 of 3

Record: 1 of 115

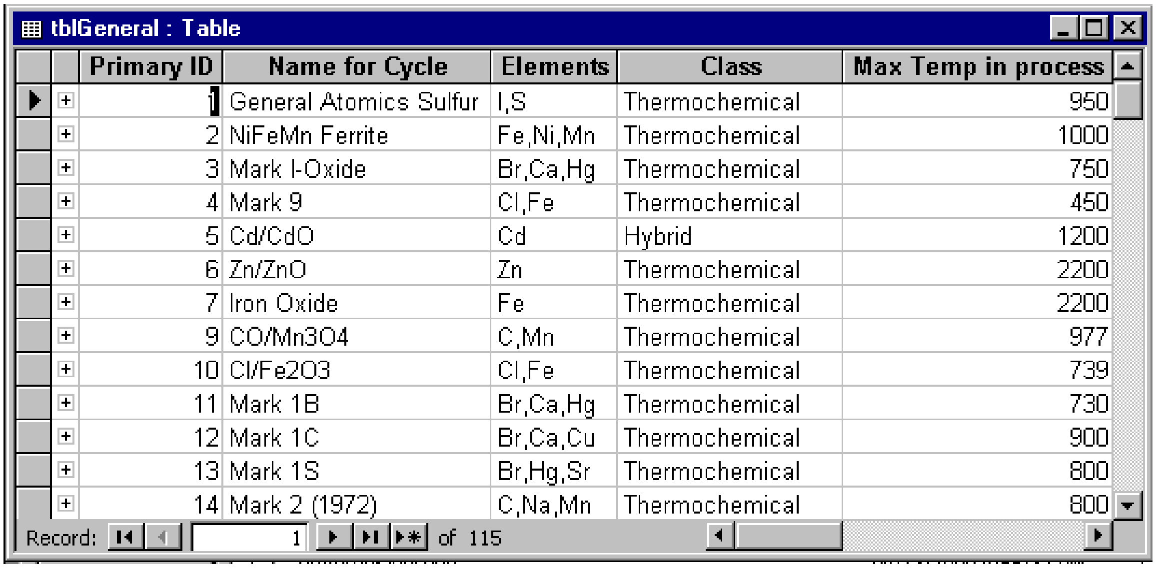
Fig. 4. Main data window for database.

allowed for papers, in which multiple cycles appeared, to be included in the database only once. Author IDs were simply the author's last name followed by the first two initials (Showalter, S.K.), this allowed for authors which appeared on multiple papers to be represented in the database uniquely. Rules were developed for addition of reactions to the database so that repetition could be easily identified. Reactants as well as products in each reaction were arranged in alphabetical order with H_2, H_2O and O_2 added to the end of the reactants or products in this order so as not to influence the naming convention used for the reaction. The reaction ID consisted of the first compound in the reactants followed by a number if there were multiple reactions with the same starting compound. Therefore, all of the reactions were in a common format and it was simple to identify replicates by inspection. All data that was available to us was entered into the database however, many fields were left blank due to lack of information.

Many of the cycles have been the subjects of previous review articles. Data for these cycles was entered directly into the cycle database and, as the literature search identified additional cycles, they were added to the cycle database. Basic bibliographic data for each additional literature source, referring to a particular cycle, was added to the cycle database and linked to the cycle.

Data was entered into the database through the following procedure:

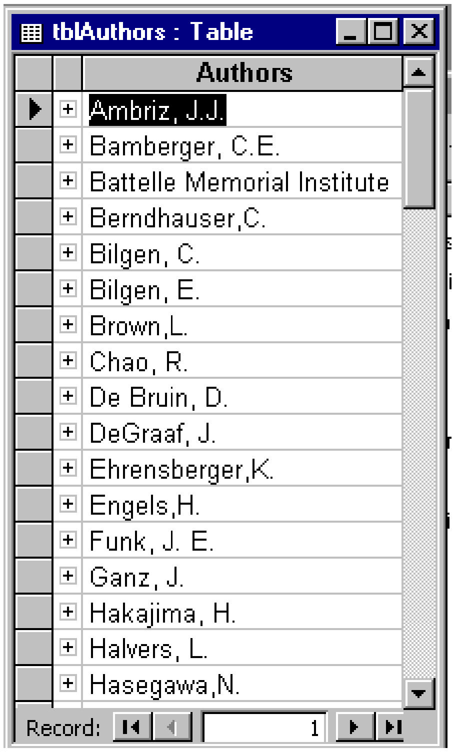
1. The cycle is first identified from a reference, compared with the general table database entries to determine if it is unique, then the general table information is entered (Fig. 5).



Primary ID	Name for Cycle	Elements	Class	Max Temp in process
1	General Atomics Sulfur	I,S	Thermochemical	950
2	NiFeMn Ferrite	Fe,Ni,Mn	Thermochemical	1000
3	Mark I-Oxide	Br,Ca,Hg	Thermochemical	750
4	Mark 9	Cl,Fe	Thermochemical	450
5	Cd/CdO	Cd	Hybrid	1200
6	Zn/ZnO	Zn	Thermochemical	2200
7	Iron Oxide	Fe	Thermochemical	2200
9	CO/Mn3O4	C,Mn	Thermochemical	977
10	Cl/Fe2O3	Cl,Fe	Thermochemical	739
11	Mark 1B	Br,Ca,Hg	Thermochemical	730
12	Mark 1C	Br,Ca,Cu	Thermochemical	900
13	Mark 1S	Br,Hg,Sr	Thermochemical	800
14	Mark 2 (1972)	C,Na,Mn	Thermochemical	800

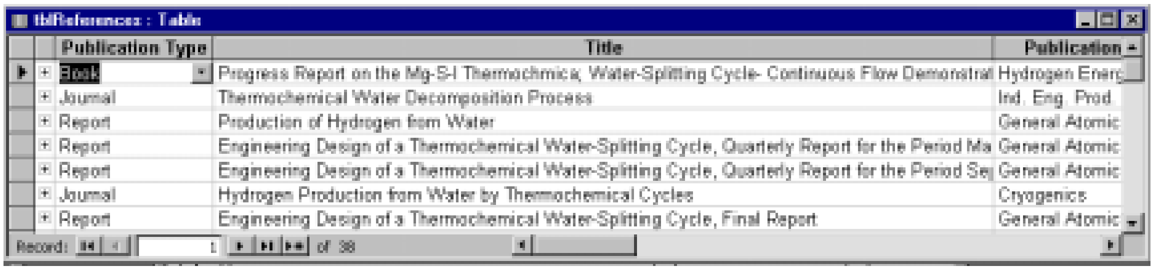
Fig. 5. General table (not all fields shown).

2. Next the authors are compared to the available authors and if they are not represented then they are added to the authors table (Fig. 6).
3. Next the reference is added to the references table and assigned a unique reference ID (Fig. 7).
4. The author junction table is then used to join the author ID with the reference ID (Fig. 8).



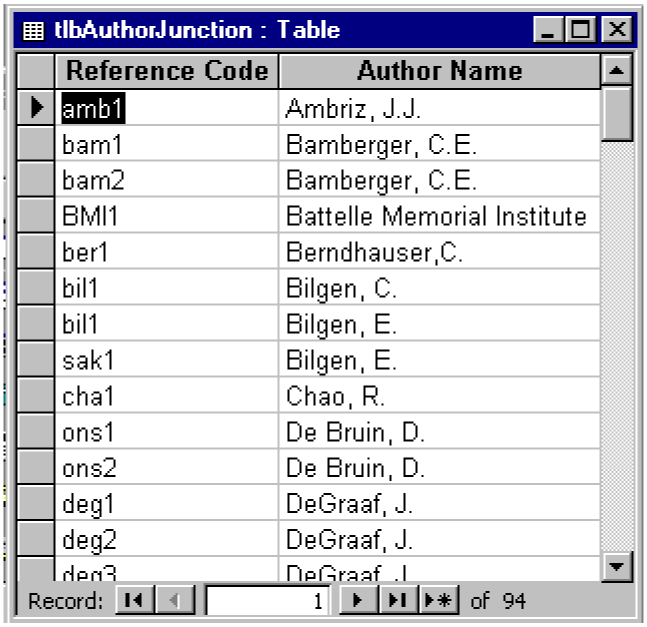
Authors
Ambriz, J.J.
Bamberger, C.E.
Battelle Memorial Institute
Berndhauser,C.
Bilgen, C.
Bilgen, E.
Brown,L.
Chao, R.
De Bruin, D.
DeGraaf, J.
Ehrensberger,K.
Engels,H.
Funk, J. E.
Ganz, J.
Hakajima, H.
Halvers, L.
Hasegawa,N.

Fig. 6. Author table.



Publication Type	Title	Publication
Book	Progress Report on the Mg-S-I Thermochmica; Water-Splitting Cycle- Continuous Flow Demonstrat	Hydrogen Ener
Journal	Thermochemical Water Decomposition Process	Ind. Eng. Prod
Report	Production of Hydrogen from Water	General Atomic
Report	Engineering Design of a Thermochemical Water-Splitting Cycle, Quarterly Report for the Period Ma	General Atomic
Report	Engineering Design of a Thermochemical Water-Splitting Cycle, Quarterly Report for the Period Se	General Atomic
Journal	Hydrogen Production from Water by Thermochemical Cycles	Cryogenics
Report	Engineering Design of a Thermochemical Water-Splitting Cycle, Final Report	General Atomic

Fig. 7. Reference table (not all fields shown)

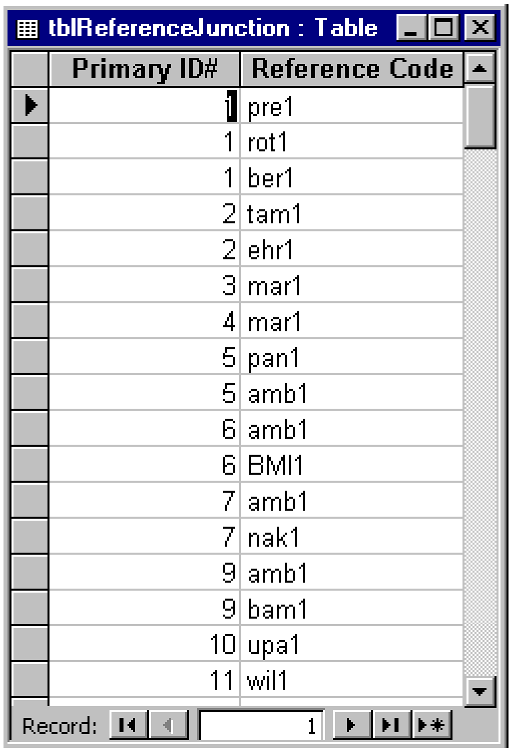


Reference Code	Author Name
amb1	Ambriz, J.J.
bam1	Bamberger, C.E.
bam2	Bamberger, C.E.
BMI1	Battelle Memorial Institute
ber1	Berndhauser,C.
bil1	Bilgen, C.
bil1	Bilgen, E.
sak1	Bilgen, E.
cha1	Chao, R.
ons1	De Bruin, D.
ons2	De Bruin, D.
deg1	DeGraaf, J.
deg2	DeGraaf, J.
deg3	DeGraaf, J.

Fig. 8. Author junction to reference table.

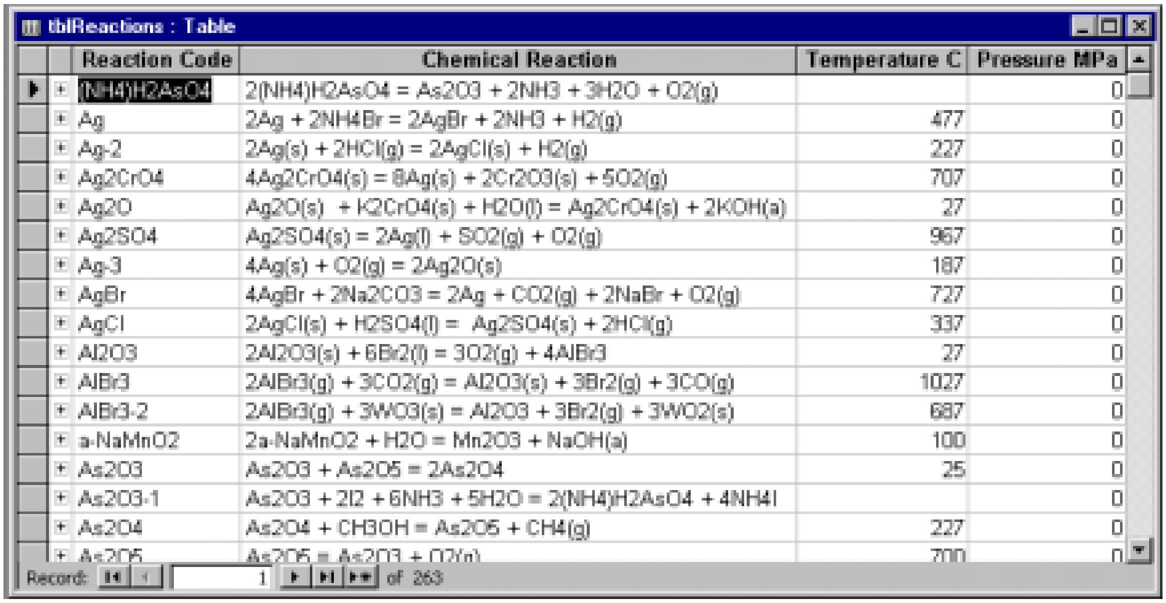
5. The reference junction table is then used to join the reference ID to the general table (primary ID) entry (Fig. 9).
6. Finally the reactions in the cycle are rearranged to fit our format (as described previously), checked against the reaction table to determine if they are represented in the table, balanced, and finally normalized to remove all fractional exponents. If not present they are entered and assigned a reaction ID into the reaction table along with any temperature or pressure information (Fig. 10).
7. The reaction IDs are then joined to the general table through the reaction junction table.
8. The final step is to determine the fractional exponent that needs to be multiplied through each reaction in a cycle to normalize all of the reaction against the decomposition of one mole of water ($H_2O \rightarrow H_2(g) + {}^1/_2\, O_2(g)$). This number is then added to the reaction junction table (Fig. 11).

This procedure allowed us to generate a database of information that could be easily searched and updated allowing us to call up information on demand for our various selection requirements.



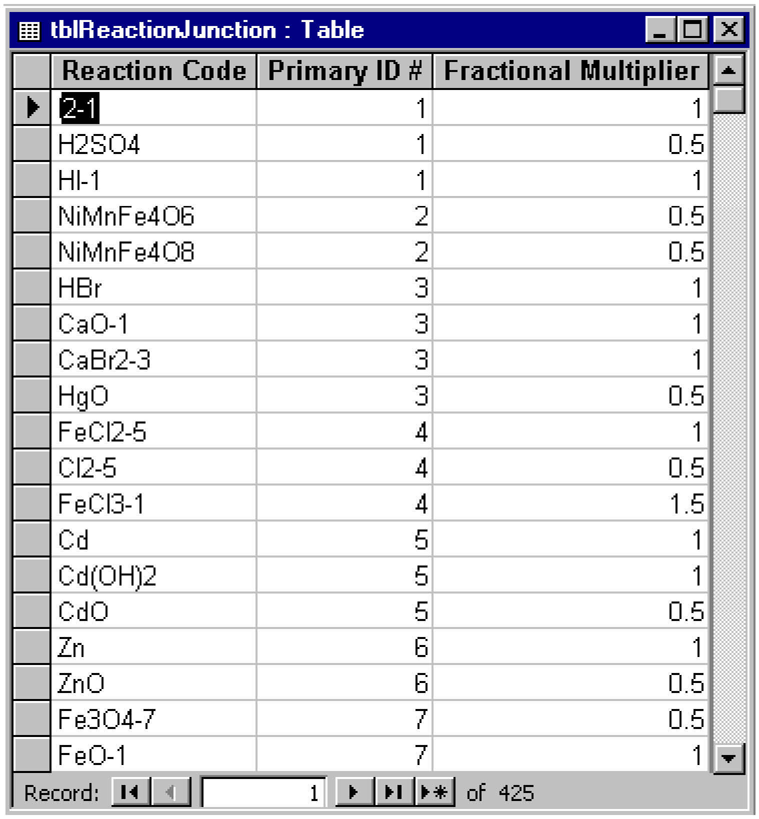
Primary ID#	Reference Code
1	pre1
1	rot1
1	ber1
2	tam1
2	ehr1
3	mar1
4	mar1
5	pan1
5	amb1
6	amb1
6	BMI1
7	amb1
7	nak1
9	amb1
9	bam1
10	upa1
11	wil1

Fig. 9. Reference junction to general table.



Reaction Code	Chemical Reaction	Temperature C	Pressure MPa
(NH4)H2AsO4	2(NH4)H2AsO4 = As2O3 + 2NH3 + 3H2O + O2(g)		0
Ag	2Ag + 2NH4Br = 2AgBr + 2NH3 + H2(g)	477	0
Ag-2	2Ag(s) + 2HCl(g) = 2AgCl(s) + H2(g)	227	0
Ag2CrO4	4Ag2CrO4(s) = 8Ag(s) + 2Cr2O3(s) + 5O2(g)	707	0
Ag2O	Ag2O(s) + K2CrO4(s) + H2O(l) = Ag2CrO4(s) + 2KOH(a)	27	0
Ag2SO4	Ag2SO4(s) = 2Ag(l) + SO2(g) + O2(g)	967	0
Ag-3	4Ag(s) + O2(g) = 2Ag2O(s)	187	0
AgBr	4AgBr + 2Na2CO3 = 2Ag + CO2(g) + 2NaBr + O2(g)	727	0
AgCl	2AgCl(s) + H2SO4(l) = Ag2SO4(s) + 2HCl(g)	337	0
Al2O3	2Al2O3(s) + 6Br2(l) = 3O2(g) + 4AlBr3	27	0
AlBr3	2AlBr3(g) + 3CO2(g) = Al2O3(s) + 3Br2(g) + 3CO(g)	1027	0
AlBr3-2	2AlBr3(g) + 3WO3(s) = Al2O3 + 3Br2(g) + 3WO2(s)	687	0
a-NaMnO2	2a-NaMnO2 + H2O = Mn2O3 + NaOH(a)	100	0
As2O3	As2O3 + As2O5 = 2As2O4	25	0
As2O3-1	As2O3 + 2I2 + 6NH3 + 5H2O = 2(NH4)H2AsO4 + 4NH4I		0
As2O4	As2O4 + CH3OH = As2O5 + CH4(g)	227	0
As2O5	As2O5 = As2O3 + O2(g)	700	0

Fig. 10. Reaction table.



Reaction Code	Primary ID #	Fractional Multiplier
2-1	1	1
H2SO4	1	0.5
HI-1	1	1
NiMnFe4O6	2	0.5
NiMnFe4O8	2	0.5
HBr	3	1
CaO-1	3	1
CaBr2-3	3	1
HgO	3	0.5
FeCl2-5	4	1
Cl2-5	4	0.5
FeCl3-1	4	1.5
Cd	5	1
Cd(OH)2	5	1
CdO	5	0.5
Zn	6	1
ZnO	6	0.5
Fe3O4-7	7	0.5
FeO-1	7	1

Fig. 11. Reaction junction to general table.

4. LITERATURE SEARCH

The literature survey was designed to locate substantially all thermochemical water-splitting cycles that have been proposed in the open literature. Keywords were chosen and test searches were made using inexpensive databases as a means of testing search strategies. Thermochemical generation of hydrogen is usually referred to, by those who practice the art, as water-splitting. It was quickly determined that searches based upon water-splitting and "water splitting" lead to many thousands of hits — few of which were concerned with thermochemical water-splitting. Inspection of the titles showed a large number of biological, biochemical and photochemical articles and numerous titles dealing with corrosion and radiolysis. Moreover, some authors do not use the term water-splitting. Attempts to limit the search, by exclusion of biological and photochemical terms (Boolean NOT) exceeded the capabilities of the search engines before a significant reduction in number of hits was realized. It has proven to be much more profitable to build up a search criteria using inclusive criteria (Boolean AND/OR). The primary limit on the search has been the requirement of the inclusion of the term "thermochemical".

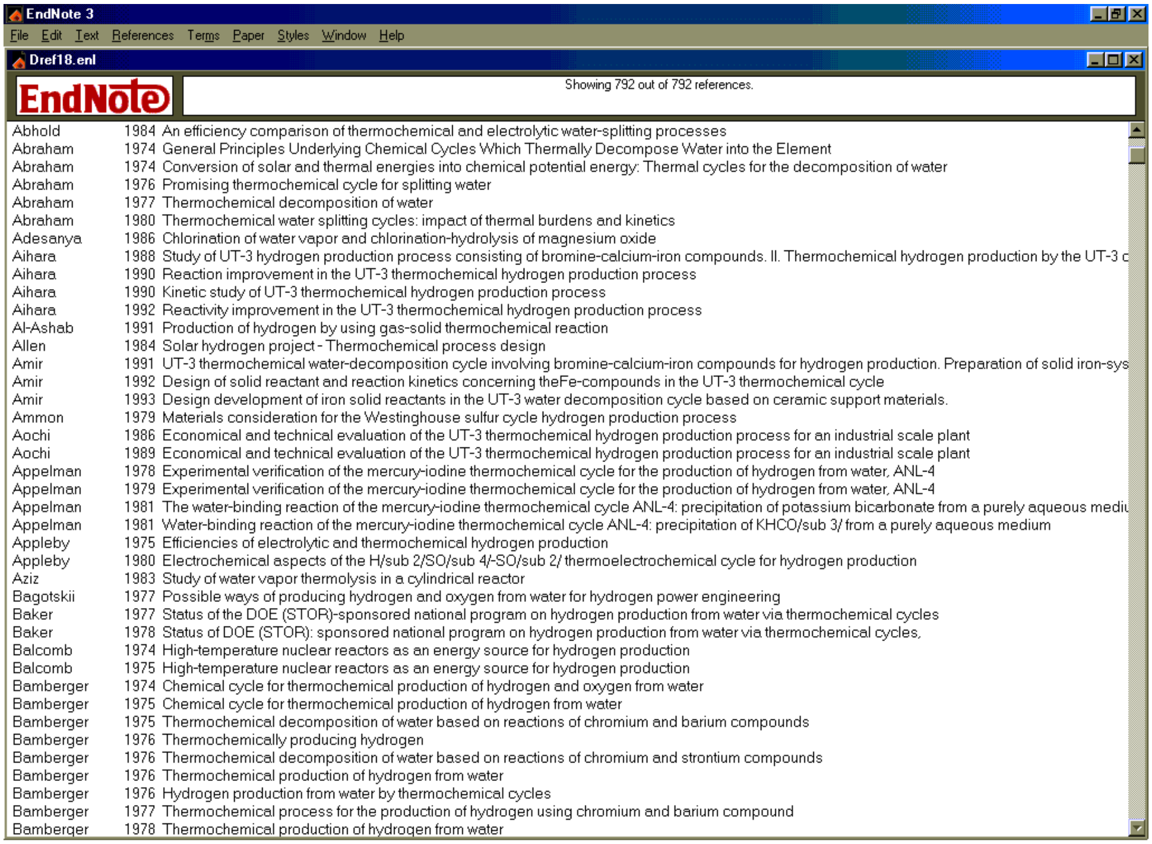
Chemical Abstracts Service (of the American Chemical Society) provides convenient access to many databases. Searching a large number of different databases can be very expensive and may produce a large number of redundant references to a single publication. The web site stnweb.cas.org allows one to simultaneously search a large number of databases at no cost, but the only results provided are the number of hits. This free search does allow one to quickly and inexpensively test various search strategies. Various Boolean searches were made of the CHEMENG cluster of databases in an attempt to optimize the search string and select the databases to be used for the "real" search. The search term ({water-splitting or water splitting or [(hydrogen or H_2) and (production or generation)]} and thermochemical) appeared to give very good results. The results from the databases showing a significant number of hits are given in Table 1.

The CAPLUS database was subjected to a full data retrieval search and over 50% of the hits are for papers related to thermochemical water-splitting. From the descriptors given for the various databases, it is likely that full searches of these databases, with the exception of NTIS, will result in hits that either duplicate hits resulting from the CAPLUS search or references previously entered into the EndNote literature database.

An example of an EndNote screen taken from our database is shown in Fig. 12. If additional information, such as an abstract is available it is displayed as shown in Fig. 13. More information about EndNote can be found at their website [5]. The formal search

TABLE 1
DATABASE HIT RESULTS

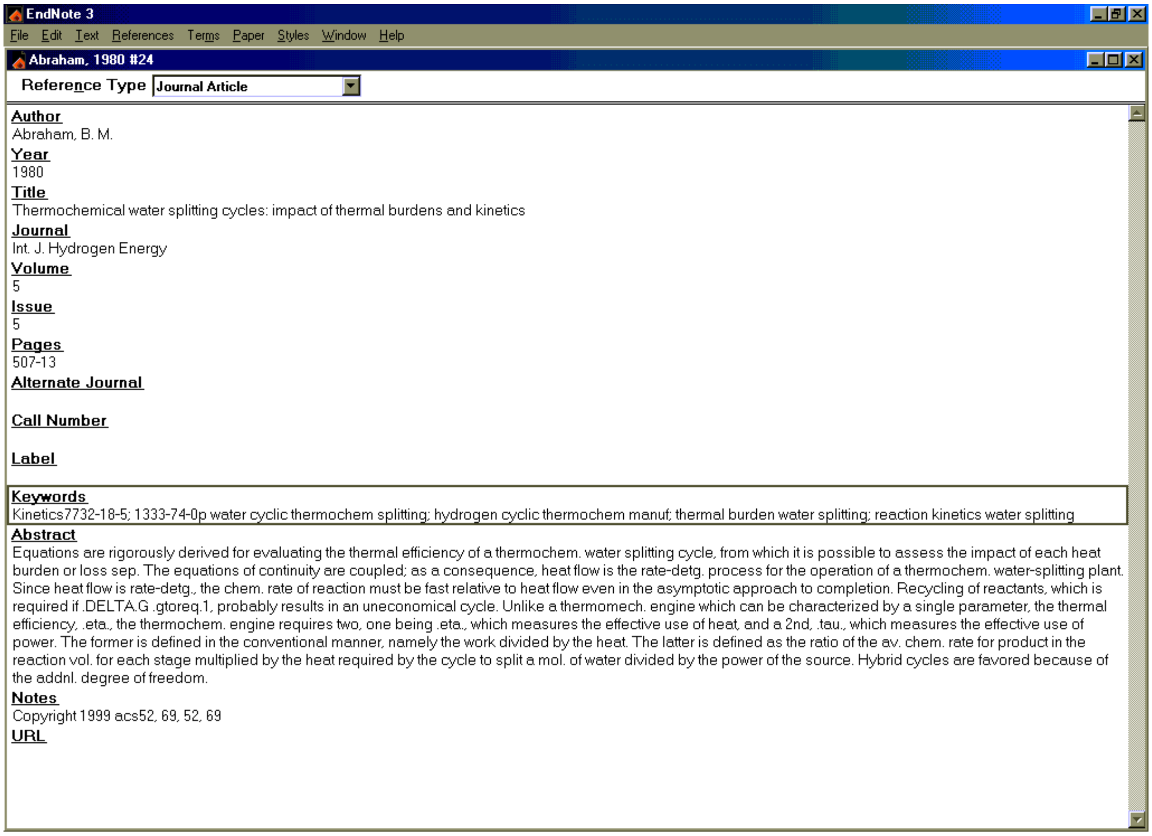
Hits	Databases	Description
905	CAPLUS	Chemical Abstracts Plus
448	COMPENDEX	COMPuterized ENgineering InDEX
440	NTIS	National Technical Information Service
322	INSPEC	The Database for Physics, Electronics and Computing. INSPEC corresponds to Physics Abstracts, Electrical & Electronics Abstracts, Computer & Control Abstracts, and Business Automation.
232	SCISEARCH	Science Citation Index Expanded
68	CEABA	Chemical Engineering And Biotechnology Abstracts
33	PROMT	Predicasts Overview of Markets and Technology — abstracts trade and business journals
28	INSPHYS	INSPHYS is a supplementary file to the INSPEC database. It contains those records from the former PHYS File from 1979 through 1994 that do not appear in INSPEC



Showing 792 out of 792 references.

Abhold	1984	An efficiency comparison of thermochemical and electrolytic water-splitting processes
Abraham	1974	General Principles Underlying Chemical Cycles Which Thermally Decompose Water into the Element
Abraham	1974	Conversion of solar and thermal energies into chemical potential energy: Thermal cycles for the decomposition of water
Abraham	1976	Promising thermochemical cycle for splitting water
Abraham	1977	Thermochemical decomposition of water
Abraham	1980	Thermochemical water splitting cycles: impact of thermal burdens and kinetics
Adesanya	1986	Chlorination of water vapor and chlorination-hydrolysis of magnesium oxide
Aihara	1988	Study of UT-3 hydrogen production process consisting of bromine-calcium-iron compounds. II. Thermochemical hydrogen production by the UT-3 c
Aihara	1990	Reaction improvement in the UT-3 thermochemical hydrogen production process
Aihara	1990	Kinetic study of UT-3 thermochemical hydrogen production process
Aihara	1992	Reactivity improvement in the UT-3 thermochemical hydrogen production process
Al-Ashab	1991	Production of hydrogen by using gas-solid thermochemical reaction
Allen	1984	Solar hydrogen project - Thermochemical process design
Amir	1991	UT-3 thermochemical water-decomposition cycle involving bromine-calcium-iron compounds for hydrogen production. Preparation of solid iron-sys
Amir	1992	Design of solid reactant and reaction kinetics concerning theFe-compounds in the UT-3 thermochemical cycle
Amir	1993	Design development of iron solid reactants in the UT-3 water decomposition cycle based on ceramic support materials.
Ammon	1979	Materials consideration for the Westinghouse sulfur cycle hydrogen production process
Aochi	1986	Economical and technical evaluation of the UT-3 thermochemical hydrogen production process for an industrial scale plant
Aochi	1989	Economical and technical evaluation of the UT-3 thermochemical hydrogen production process for an industrial scale plant
Appelman	1978	Experimental verification of the mercury-iodine thermochemical cycle for the production of hydrogen from water, ANL-4
Appelman	1979	Experimental verification of the mercury-iodine thermochemical cycle for the production of hydrogen from water, ANL-4
Appelman	1981	The water-binding reaction of the mercury-iodine thermochemical cycle ANL-4: precipitation of potassium bicarbonate from a purely aqueous mediu
Appelman	1981	Water-binding reaction of the mercury-iodine thermochemical cycle ANL-4: precipitation of KHCO/sub 3/ from a purely aqueous medium
Appleby	1975	Efficiencies of electrolytic and thermochemical hydrogen production
Appleby	1980	Electrochemical aspects of the H/sub 2/SO/sub 4/-SO/sub 2/ thermoelectrochemical cycle for hydrogen production
Aziz	1983	Study of water vapor thermolysis in a cylindrical reactor
Bagotskii	1977	Possible ways of producing hydrogen and oxygen from water for hydrogen power engineering
Baker	1977	Status of the DOE (STOR)-sponsored national program on hydrogen production from water via thermochemical cycles
Baker	1978	Status of DOE (STOR): sponsored national program on hydrogen production from water via thermochemical cycles,
Balcomb	1974	High-temperature nuclear reactors as an energy source for hydrogen production
Balcomb	1975	High-temperature nuclear reactors as an energy source for hydrogen production
Bamberger	1974	Chemical cycle for thermochemical production of hydrogen and oxygen from water
Bamberger	1975	Chemical cycle for thermochemical production of hydrogen from water
Bamberger	1975	Thermochemical decomposition of water based on reactions of chromium and barium compounds
Bamberger	1976	Thermochemically producing hydrogen
Bamberger	1976	Thermochemical decomposition of water based on reactions of chromium and strontium compounds
Bamberger	1976	Thermochemical production of hydrogen from water
Bamberger	1976	Hydrogen production from water by thermochemical cycles
Bamberger	1977	Thermochemical process for the production of hydrogen using chromium and barium compound
Bamberger	1978	Thermochemical production of hydrogen from water

Fig. 12. Screen shot of EndNote database of literature survey results.



Reference Type: Journal Article

Author
Abraham, B. M.

Year
1980

Title
Thermochemical water splitting cycles: impact of thermal burdens and kinetics

Journal
Int. J. Hydrogen Energy

Volume
5

Issue
5

Pages
507-13

Alternate Journal

Call Number

Label

Keywords
Kinetics7732-18-5; 1333-74-0p water cyclic thermochem splitting; hydrogen cyclic thermochem manuf; thermal burden water splitting; reaction kinetics water splitting

Abstract
Equations are rigorously derived for evaluating the thermal efficiency of a thermochem. water splitting cycle, from which it is possible to assess the impact of each heat burden or loss sep. The equations of continuity are coupled; as a consequence, heat flow is the rate-detg. process for the operation of a thermochem. water-splitting plant. Since heat flow is rate-detg., the chem. rate of reaction must be fast relative to heat flow even in the asymptotic approach to completion. Recycling of reactants, which is required if .DELTA.G .gtoreq.1, probably results in an uneconomical cycle. Unlike a thermomech. engine which can be characterized by a single parameter, the thermal efficiency, .eta., the thermochem. engine requires two, one being .eta., which measures the effective use of heat, and a 2nd, .tau., which measures the effective use of power. The former is defined in the conventional manner, namely the work divided by the heat. The latter is defined as the ratio of the av. chem. rate for product in the reaction vol. for each stage multiplied by the heat required by the cycle to split a mol. of water divided by the power of the source. Hybrid cycles are favored because of the addnl. degree of freedom.

Notes
Copyright 1999 acs52, 69, 52, 69

URL

Fig. 13. Screen shot: Individual entry in EndNote database of literature survey results.

was completed by performing similar searches on the NTIS database, the DOE PubSCIENCE database [6] and the IBM Patent Server [7]. The results were added to the literature database. The EndNote database contains 822 entries, after purging duplicate and irrelevant entries.

Interest in thermochemical water splitting has varied greatly with time. Figure 14 indicates when the references in the database were published. The initial interest, in the early 1960s [8], was by the military, which was interested in the use of a portable nuclear reactor to provide logistical support, but interest quickly switched to civilian uses. Interest boomed in the 1970s at the time of the Arab Oil Crisis but petered out with the onset of cheap oil and plentiful natural gas. The last review of the subject was published in 1988 [9], just as the major funding in this area decreased worldwide. Since that time, about eight thermochemical water-splitting related papers have been published per year. Most of the continuing work takes place in Japan where dependence upon foreign energy sources continues to be of national concern.

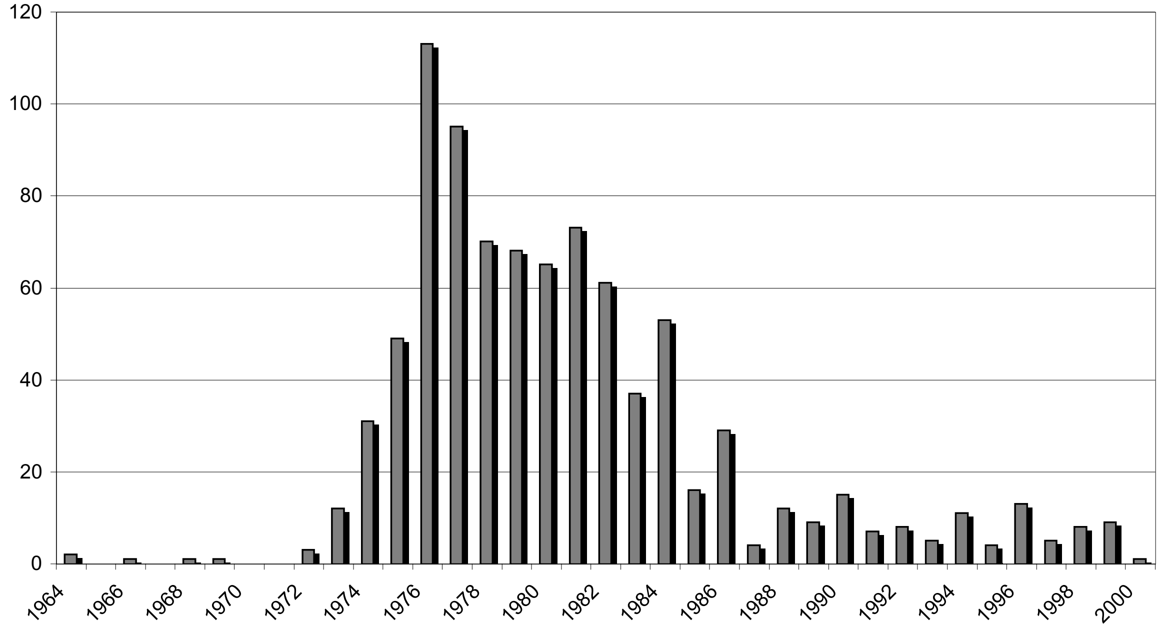


Fig. 14. Publications by year of issue.

5. PRELIMINARY SCREENING CRITERIA

As expected, the literature search turned up a large number of cycles (115), far too many to analyze in depth. In order to establish objective screening criteria, with which to reduce the number of cycles to a manageable number, it was necessary to establish meaningful and quantifiable criteria. The criteria given in Table 2 were presented in the original proposal. Our first task was to determine if, indeed, these were the appropriate criteria and if so, to establish metrics by which each proposed cycle could be evaluated according to each criterion. We also needed to establish weighing factors for each criterion with which to establish a final weighted score for each cycle.

TABLE 2
PROPOSED INITIAL SCREENING CRITERIA

Criteria	Impact
1. Number of reactions and/or separation steps in the cycle	Smaller number indicated reduces process complexity and cost
2. Number of elements in the cycle	Smaller number indicates less cost/complexity in element recovery
3. Cost and availability of process chemicals	There may be strategic availability issues
4. Corrosiveness of the process media and availability/cost of materials of construction and cost must be considered	Improved materials of construction may allow consideration of processes previously dismissed yet effect on hydrogen production efficiency
5. Are non-stationary solid reactants involved?	Bulk movement of solid reactants greatly increases processing difficulty and cost
6. Projected effect of higher temperatures on cost	This addresses the potential for higher hydrogen production cycle efficiency and temperatures in future nuclear reactors
7. Environmental, Safety and Health (ESH) considerations	Are there basic environmental safety and health issues with the cycle?
8. Amount of research done	Has the scientific basis of this cycle been verified or is it a new process?
9. Was at least a bench scale continuous flow model operated	Indicates the relative maturity of a process
10. Are efficiency and/or cost figures available? How good are they?	Indicates a significant amount of engineering design work

The criteria ultimately agreed upon are very similar to those originally proposed. Table 3 gives the basis for selecting the screening criteria and the metrics finally chosen. The translation of each metric, to a score based on the metric, is given in Table 4. Where possible the metrics are calculated from data, otherwise they are a consensus judgment of the principal investigators. Equal weighting was given to each criterion in calculating the final score for each process.

One of the original criteria was left out of the methodology because a simple metric could not be devised that would permit a score to be calculated from first principles. We decided that Environmental, Safety and Health (ES&H) concerns would be taken into account on a case by case basis after the list of cycles was limited using the numerical screening process.

TABLE 3
RATIONAL FOR DEVELOPMENT OF FIRST ROUND SCREENING CRITERIA

	Desirable Characteristic	Rational	Metric
1	Higher ranked cycles will have a minimum number of chemical reactions steps in the cycle.	A smaller number of chemical reactions indicates a simpler process and lower costs.	Score is based on number of chemical reactions.
2	Higher ranked cycles will have a minimum number of separation steps in the cycle.	A smaller number of chemical separations indicates a simpler process and lower costs.	Score is based on number of chemical separations, excluding simple phase separation.
3	Higher ranked cycles will have a minimum number of elements in the cycle.	A smaller number of chemical elements indicates a simpler process and lower costs.	Score is based on number of elements, excluding oxygen and hydrogen
4	Higher ranked cycles will employ elements which are abundant in the earth's crust, oceans and atmosphere.	Use of abundant elements will lower the cost and permit the chosen technology to be implemented on a large scale. There may be strategic availability issues.	Score is based on least abundant element in cycle.
5	Higher ranked cycles will minimize the use of expensive materials of construction by avoiding corrosive chemical systems, particularly in heat exchangers.	Improved materials of construction may allow consideration of processes previously dismissed yet the effect of materials cost on hydrogen production efficiency and cost must be considered.	Score is based on the relative corrosiveness of the process solutions.
6	Higher ranked cycles will minimize the flow of solids.	Chemical plant costs are considerably higher for solids processing plants. Flow of solid materials also corresponds to increased maintenance costs due to wear and to increased downtime due to blockage and unscheduled equipment failure.	Score is based on minimization of solid flow problems.
7	Higher ranked cycles will have maximum heat input temperature compatible with high temperature heat transfer materials.	High thermal efficiency cannot be realized without a high temperature heat input to the water-splitting process. The limit on temperature will be the thermal and mechanical performance of the heat transfer material separating the reactor coolant from the process stream requiring the highest temperature.	Score is based on the high temperature heat input to the process being close to that delivered by an advanced nuclear reactor.
8	Higher ranked cycles will have been the subject of many papers from many authors and institutions.	Cycles that have been thoroughly studied in the literature have a lower probability of having undiagnosed flaws.	Score will be based on the number of papers published dealing with the cycle.
9	Higher ranked cycles will have been tested at a moderate or large scale,	Relatively mature processes will have had their unit operations tested at relatively large scale. Processes for which the basic chemistry has not been verified are suspect.	Score will be based on the degree to which the chemistry of the cycle has been actually demonstrated and not just postulated.
10	Higher ranked cycles will have good efficiency and cost data available.	A significant amount of engineering design work is necessary to estimate process efficiencies and production costs. Note: cost estimates in the absence of efficiency calculations are meaningless and will not be considered.	Score will be based on the degree to which efficiencies and cost have been estimated.

TABLE 4
METRICS USED TO SCORE PROCESSES. FOR EACH METRIC, THE PROCESS RECEIVES THE SCORE INDICATED. THE PROCESS SCORE IS THE SUM OF THE INDIVIDUAL SCORES

Metric ⇓ Score ⇒	0	1	2	3	4	5	6	7	8	9	10
1. Number of chemical reactions	6	-	-	5	-	-	4	-	-	3	2
2. Number of chemical separation steps	10	9	8	7	6	5	4	3	2	1	0
3. Number of elements – 2	7		6	-	5	-	4	-	3	2	1
4. Least abundant element in process	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
5. Relative corrosiveness of process solutions†	Very corrosive, e.g. *aqua* regia				Moderately corrosive, e.g. sulfuric acid						Not corrosive
6. Degree to which process is continuous and flow of solids is minimized	Batch flow of solids			Continuous flow of solids		Flow of gases or liquids through packed beds				Continuous flow of liquids and gases	
7. Maximum temperature in process (°C)	<300 or <1300	300–350 or 1250–1300	350–400 or 1200–1250	400–450 or 1150–1200	450–500 or 1100–1150	500–550 or 1050–1100	550–600 or 1000–1050	600–650 or 950–1000	650–700 or 900–950	700–750 or 850–900	750–850
8. Number of published references to cycle†	1 paper	A few papers			Many papers				Extensive literature base		
9. Degree to which chemistry of cycle has been demonstrated†	No laboratory work			Test tube scale testing			Bench scale testing				Pilot plant scale testing
10. Degree to which good efficiency and cost data are available†	No efficiency estimate available		Thermodynamic efficiency estimated from elementary reactions.		Thermodynamic efficiency estimate based on rough flowsheet		Thermodynamic efficiency calculation based on detailed flow sheet		Detailed cost calculations, based on detailed flowsheets available from one or more independent sources.		

†Interpolate scores between defined scale points.

6. PRELIMINARY SCREENING PROCESS

The preliminary screening process consisted of applying the metrics to each process and summing the scores to get an overall score for each process. Some of the metrics can be easily calculated but for the others, value judgments are required. The three principal investigators jointly went over these aspects of all 115 cycles to generate a consensus score for each cycle and for each metrics requiring a judgment call. The scores for Metrics 1, 2, 3, 4 and 7 are readily evaluated with little subjective judgment required. The other metrics required a consensus judgment.

Metric 1 — Number of Chemical Reactions. Counting the number of chemical reactions is usually easy. An exception is when two or more chemical reactions occur sequentially in a single processing operation. In this case, we considered there to be just one reaction, for the purpose of calculating the score. This question arises primarily for cycles involving the decomposition of sulfuric acid. Most authors considered the reaction to be

(2) $H_2SO_4 \rightarrow SO_2 + H_2O + {}^1/_2O_2$

whereas others, attempting to be more precise, considered there to be two reactions

(2a) $H_2SO_4 \rightarrow H_2O + SO_3$

followed by

(2b) $SO_3 \rightarrow SO_2 + {}^1/_2O_2$.

Since both reactions occur sequentially in a single heat exchanger/reactor system, without any intermediate separations, we considered there to be one reaction, independent of the way the cycle was described in the literature.

Metric 2 — Number of Chemical Separation Steps. The number of separations for a cycle was determined from the number of separations required for each chemical reaction. Each chemical reaction is assumed to yield a mixture of its reactants and products. After phase separation, for each phase, there is one less separation than there are components, if the components must be separated before the next reaction. As an example, consider the reactions of the UT-3 cycle [10].

(5) $2Br_2(g) + 2CaO(s) \rightarrow 2CaBr_2(s) + {}^1/_2O_2(g)$ (672°C)

(6) $3FeBr_2(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 6HBr + H_2(g)$ (560°C)

(7) $CaBr_2(s) + H_2O(g) \rightarrow CaO(s) + 2HBr(g)$ (760°C)

(8) $Fe_3O_4(s) + 8HBr(g) \rightarrow Br_2(g) + 3FeBr_2(s) + 4H_2O(g)$ (210°C)

For this cycle, the solid reactants remain in fixed beds with the gas flow cycled between the beds as the temperatures are changed. The solids are never separated, even if the reaction is not driven to completion, and so solid separations do not contribute to the score. Reaction (5) includes two gaseous species, bromine and oxygen, and therefore one separation. Reaction (6) has three gaseous species, water, hydrogen bromide and hydrogen, and thus two separations. Reactions (7) and (8) have two and three gaseous species and one and two separations giving a potential total of six separations for the process. We recognized that the hydrogen bromide/water mixtures from Reactions (6) and (7) could be fed to Reaction (8) without separation, leaving three separations for a score of seven for this metric. Similar analyses were made for each cycle.

Metric 3 — Number of Elements. Every element found in any reaction of the cycle was listed and counted. Oxygen and hydrogen, which occur in every cycle, were ignored. Catalysts, which are not indicated in the reaction equations, were also ignored.

Metric 4 — Elemental Abundance. Elements were ordered based on their atomic abundance in the earth’s crust and separated into groups differing by roughly an order of magnitude in abundance. An exception is nitrogen, which, based on its abundance in the atmosphere, was grouped with more abundant elements. The score was then based on the least abundant element employed in the cycle.

Metric 5 — Corrosive Chemicals. Cycles were rated based on the most corrosive materials in the process. If no corrosive materials are involved the cycles were given a 10. No cycle was rated worse than 5, which was defined as equivalent to sulfuric acid.

Metric 6 — Solids Flow. Cycles were separated into four groups: (1) cycles involving only gases and liquids, (2) cycles in which solids remained in stationary beds, (3) cycles in which solids flow continuously and (4) cycles in which solids remain in stationary beds part of the time and are moved at other times. We assumed that solids could be processed in static beds if only gas solid reactions were involved and all solid reactants resulted in solid products. We assumed that batch flow of solids would be necessary if liquids were converted to solids. It might not be strictly necessary that there be batch flow of solids in this case but the complications would be equally onerous and the score would be the same.

Metric 7 — Maximum Cycle Temperature. The maximum cycle temperature was another parameter requiring analysis. The score was reduced if the maximum temperature was either above or below that deemed optimum for an advanced high-temperature nuclear reactor. We used the temperatures given by the cycle proponents except where that would lower the score or when the value suggested produced a large positive for a non-electrolytic reaction. As an example of the former, Reaction (1) is part of several different cycles. The temperature of this reaction is quoted anywhere between 700°C and 1100°C. This reaction actually represents the sequence of Reactions 2(a) and 2(b). The Gibbs free energy of Reaction 2(b) changes relatively little over the range from 700°C to 1100°C so the net result of changing the temperature is to shift the equilibrium towards the products. It is not reasonable to give different cycles different scores based on use of the same high-temperature chemical reaction. In cases like this, we gave the maximum reasonable score to all cycles. In cases where the cycle proponents gave a temperature for which the reaction was non-spontaneous, i.e., it has a very positive Gibbs free energy, we assigned the temperature where the free energy was near zero. We used the computer program HSC Chemistry 4.0 [11] to calculate the free energy of each reaction as a function of temperature.

Metric 8 — References. The number of publications was determined from the literature search. Most cycles had either very few publications or very many publications.

Metric 9 — Chemical Demonstration. The degree and scale to which the chemistry has been demonstrated was determined from the literature.

Metric 10 — Efficiency and Cost Data. The degree to which costs and efficiencies have been calculated was determined from the literature.

There was a significant correlation between the scores from the last three metrics. Leaving these metrics out of the scoring had little effect on which cycles scored best. This is probably because previous work has concentrated on cycles with few reactions, simple separations, available materials, which have minimal solids flow problems and which have their heat input requirements at reasonable temperatures.

7. FIRST STAGE SHORT LIST

The screening criteria were applied to all 115 cycles and the results were sorted according to the total number of screening points awarded to each process. We had hoped that the totals would cluster in to high scoring and low scoring cycles to make the down selection easy, but this was not the case. We therefore somewhat arbitrarily used 50 points (out of the total possible of 100) as the cut-off score. The original goal was to retain 20–30 cycles, after down selection, for more detailed evaluation. Using 50 points as the cut-off gave over 40 cycles, which allowed us room to apply ES&H considerations as well as well as other “sanity checks”.

Three additional go/no-go tests were applied to the short list. Two cycles were eliminated for ES&H reasons in that they are based on mercury and we do not believe that it would be possible to license such a plant. Three cycles were eliminated because they require temperatures in excess of 1600°C, which places them outside the scope of processes that are compatible with advanced nuclear reactors contemplated in the next 50 years. Additionally, use of the program HSC Chemistry 4.0 [11] allowed us to analyze cycles for thermodynamic feasibility earlier in the screening process than we had originally foreseen. Seven cycles were eliminated because they had reactions that have large positive free energies that cannot be accomplished electrochemically. The final short list of 25 cycles is given in Table 5, along with their scores. One literature reference is included for each cycle. Details for these cycles are given in Table 6.

TABLE 5
SHORT LIST OF CYCLES AND THEIR SCORES

Cycle#	Name	Class	Max T	Elem	#elem	#seps	#Rxns	Rxns	Seps	Elems	Abund	Corr	Solids	Temp	Pubs	Tests	Data	Total
1	Westinghouse [12]	H	850	S	1	2	2	10	8	10	9	5	10	9	10	6	8	85
2	Ispra Mark 13 [13]	H	850	Br,S	2	3	3	9	7	9	7	5	10	9	10	6	8	80
3	UT-3 Univ. of Tokyo [8]	T	750	Br,Ca,Fe	3	3	4	6	7	8	7	5	6	10	10	10	10	79
4	Sulfur-Iodine [14]	T	800	I,S	2	3	3	9	7	9	4	5	10	10	10	6	8	78
5	Julich Center EOS [15]	T	800	Fe,S	2	3	3	9	7	9	9	9	6	10	3	3	3	68
6	Tokyo Inst. Tech. Ferrite [16]	T	1000	Fe,Mn,Na	3	2	2	10	8	8	8	10	10	6	2	2	0	64
7	Hallett Air Products 1965 [15]	H	800	Cl	1	3	2	10	7	10	10	5	10	10	0	0	0	62
8	Gaz de France [15]	T	825	K	1	3	3	9	7	10	9	5	6	10	2	2	2	62
9	Nickel Ferrite [17]	T	1000	Fe,Ni,Mn	3	0	2	10	10	8	7	10	6	6	0	3	0	60
10	Aachen Univ Julich 1972 [15]	T	800	Cr,Cl	2	3	3	9	7	9	7	5	6	10	2	2	2	59
11	Mark 1C [13]	T	900	Br,Ca,Cu	3	4	4	6	6	8	7	5	10	8	2	3	3	58
12	LASL- U [15]	T	700	C,U	2	3	3	9	7	9	4	10	6	9	1	3	0	58
13	Ispra Mark 8 [13]	T	900	Cl,Mn	2	3	3	9	7	9	8	5	3	8	3	2	3	57
14	Ispra Mark 6 [13]	T	800	Cl,Cr,Fe	3	4	4	6	6	8	7	5	6	10	2	3	3	56
15	Ispra Mark 4 [13]	T	800	Cl,Fe	2	4	4	6	6	9	10	5	0	10	3	3	3	55
16	Ispra Mark 3 [13]	T	800	Cl,V	2	3	3	9	7	9	7	5	0	10	2	3	3	55
17	Ispra Mark 2 (1972) [13]	T	800	C,Na,Mn	3	3	3	9	7	8	8	5	0	10	2	3	3	55
18	Ispra CO/Mn_3O_4 [18]	T	977	C,Mn	2	3	3	9	7	9	8	9	6	7	0	0	0	55
19	Ispra Mark 7B [13]	T	1000	Cl,Fe	2	5	5	3	5	9	10	5	10	6	0	3	3	54
20	Vanadium Chloride [19]	T	700	Cl,V	3	5	4	6	5	8	7	5	6	9	3	2	2	53
21	Ispra Mark 7A [13]	T	1000	Cl,Fe	2	5	5	3	5	9	10	5	6	6	3	3	3	53
22	GA Cycle 23 [20]	T	850	S	2	4	5	3	6	9	9	5	10	9	0	0	0	51
23	US –Chlorine [15]	T	993	Cl,Cu	2	3	3	9	7	9	7	6	5	7	0	0	0	50
24	Ispra Mark 9 [13]	T	450	Cl,Fe	2	8	3	9	2	9	10	5	3	4	2	3	3	50
25	Ispra Mark 6C [13]	T	800	Cl,Cr,Cu,Fe	4	5	5	3	5	6	7	5	6	10	2	3	3	50

TABLE 6
REACTION DETAILS FOR CYCLES

Cycle	Name	T/E*	T (°C)	Reaction	F†
1	Westinghouse [12]	T	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	$^1/_2$
		E	77	$SO_2(g) + 2H_2O(a) \rightarrow H_2SO_4(a) + H_2(g)$	1
2	Ispra Mark 13 [13]	T	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	$^1/_2$
		E	77	$2HBr(a) \rightarrow Br_2(a) + H_2(g)$	1
		T	77	$Br_2(l) + SO_2(g) + 2H_2O(l) \rightarrow 2HBr(g) + H_2SO_4(a)$	1
3	UT-3 Univ. of Tokyo [8]	T	600	$2Br_2(g) + 2CaO \rightarrow 2CaBr_2 + O_2(g)$	$^1/_2$
		T	600	$3FeBr_2 + 4H_2O \rightarrow Fe_3O_4 + 6HBr + H_2(g)$	1
		T	750	$CaBr_2 + H_2O \rightarrow CaO + 2HBr$	1
		T	300	$Fe_3O_4 + 8HBr \rightarrow Br_2 + 3FeBr_2 + 4H_2O$	1
4	Sulfur-Iodine [14]	T	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	$^1/_2$
		T	450	$2HI \rightarrow I_2(g) + H_2(g)$	1
		T	120	$I_2 + SO_2(a) + 2H_2O \rightarrow 2HI(a) + H_2SO_4(a)$	1
5	Julich Center EOS [15]	T	800	$2Fe_3O_4 + 6FeSO_4 \rightarrow 6Fe_2O_3 + 6SO_2 + O_2(g)$	$^1/_2$
		T	700	$3FeO + H_2O \rightarrow Fe_3O_4 + H_2(g)$	1
		T	200	$Fe_2O_3 + SO_2 \rightarrow FeO + FeSO_4$	6
6	Tokyo Inst. Tech. Ferrite [16]	T	1000	$2MnFe_2O_4 + 3Na_2CO_3 + H_2O \rightarrow 2Na_3MnFe_2O_6 + 3CO_2(g) + H_2(g)$	1
		T	600	$4Na_3MnFe_2O_6 + 6CO_2(g) \rightarrow 4MnFe_2O_4 + 6Na_2CO_3 + O_2(g)$	$^1/_2$
7	Hallett Air Products 1965 [15]	T	800	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	$^1/_2$
		E	25	$2HCl \rightarrow Cl_2(g) + H_2(g)$	1
8	Gaz de France [15]	T	725	$2K + 2KOH \rightarrow 2K_2O + H_2(g)$	1
		T	825	$2K_2O \rightarrow 2K + K_2O_2$	1
		T	125	$2K_2O_2 + 2H_2O \rightarrow 4KOH + O_2(g)$	$^1/_2$
9	Nickel Ferrite [17]	T	800	$NiMnFe_4O_6 + 2H_2O \rightarrow NiMnFe_4O_8 + 2H_2(g)$	1
		T	800	$NiMnFe_4O_8 \rightarrow NiMnFe_4O_6 + O_2(g)$	$^1/_2$
10	Aachen Univ Julich 1972 [15]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	$^1/_2$
		T	170	$2CrCl_2 + 2HCl \rightarrow 2CrCl_3 + H_2(g)$	1
		T	800	$2CrCl_3 \rightarrow 2CrCl_2 + Cl_2(g)$	1
11	Ispra Mark 1C [13]	T	100	$2CuBr_2 + Ca(OH)_2 \rightarrow 2CuO + 2CaBr_2 + H_2O$	1
		T	900	$4CuO(s) \rightarrow 2Cu_2O(s) + O_2(g)$	$^1/_2$
		T	730	$CaBr_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HBr$	2
		T	100	$Cu_2O + 4HBr \rightarrow 2CuBr_2 + H_2(g) + H_2O$	1
12	LASL- U [15]	T	25	$3CO_2 + U_3O_8 + H_2O \rightarrow 3UO_2CO_3 + H_2(g)$	1
		T	250	$3UO_2CO_3 \rightarrow 3CO_2(g) + 3UO_3$	1
		T	700	$6UO_3(s) \rightarrow 2U_3O_8(s) + O_2(g)$	$^1/_2$
13	Ispra Mark 8 [13]	T	700	$3MnCl_2 + 4H_2O \rightarrow Mn_3O_4 + 6HCl + H_2(g)$	1
		T	900	$3MnO_2 \rightarrow Mn_3O_4 + O_2(g)$	$^1/_2$
		T	100	$4HCl + Mn_3O_4 \rightarrow 2MnCl_2(a) + MnO_2 + 2H_2O$	$^3/_2$
14	Ispra Mark 6 [13]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	$^1/_2$
		T	170	$2CrCl_2 + 2HCl \rightarrow 2CrCl_3 + H_2(g)$	1
		T	700	$2CrCl_3 + 2FeCl_2 \rightarrow 2CrCl_2 + 2FeCl_3$	1
		T	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	1
15	Ispra Mark 4 [13]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	$^1/_2$
		T	100	$2FeCl_2 + 2HCl + S \rightarrow 2FeCl_3 + H_2S$	1
		T	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	1
		T	800	H_2S ™ $S + H_2(g)$	1

TABLE 6
REACTION DETAILS FOR CYCLES (Continued)

Cycle	Name	T/E*	T °C	Reaction	F†
16	Ispra Mark 3 [13]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	$^1/_2$
		T	170	$2VOCl_2 + 2HCl \rightarrow 2VOCl_3 + H_2(g)$	1
		T	200	$2VOCl_3 \rightarrow Cl_2(g) + 2VOCl_2$	1
17	Ispra Mark 2 (1972) [13]	T	100	$Na_2O.MnO_2 + H_2O \rightarrow 2NaOH(a) + MnO_2$	2
		T	487	$4MnO_2(s) \rightarrow 2Mn_2O_3(s) + O_2(g)$	$^1/_2$
		T	800	$Mn_2O_3 + 4NaOH \rightarrow 2Na_2O.MnO_2 + H_2(g) + H_2O$	1
18	Ispra CO/Mn_3O_4 [18]	T	977	$6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2(g)$	$^1/_2$
		T	700	$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$	1
		T	700	$CO(g) + 2Mn_3O_4 \rightarrow C + 3Mn_2O_3$	1
19	Ispra Mark 7B [13]	T	1000	$2Fe_2O_3 + 6Cl_2(g) \rightarrow 4FeCl_3 + 3O_2(g)$	$^3/_4$
		T	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	$^3/_2$
		T	650	$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2(g)$	1
		T	350	$4Fe_3O_4 + O_2(g) \rightarrow 6Fe_2O_3$	$^1/_4$
		T	400	$4HCl + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O$	$^3/_2$
20	Vanadium Chloride [19]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	$^1/_2$
		T	25	$2HCl + 2VCl_2 \rightarrow 2VCl_3 + H_2(g)$	1
		T	700	$2VCl_3 \rightarrow VCl_4 + VCl_2$	2
		T	25	$2VCl_4 \rightarrow Cl_2(g) + 2VCl_3$	1
21	Mark 7A [13]	T	420	$2FeCl_3(l) \rightarrow Cl_2(g) + 2FeCl_2$	$^3/_2$
		T	650	$3FeCl_2 + 4H_2O(g) \rightarrow Fe_3O_4 + 6HCl(g) + H_2(g)$	1
		T	350	$4Fe_3O_4 + O_2(g) \rightarrow 6Fe_2O_3$	$^1/_4$
		T	1000	$6Cl_2(g) + 2Fe_2O_3 \rightarrow 4FeCl_3(g) + 3O_2(g)$	$^1/_4$
		T	120	$Fe_2O_3 + 6HCl(a) \rightarrow 2FeCl_3(a) + 3H_2O(l)$	1
22	GA Cycle 23 [20]	T	800	$H_2S(g) \rightarrow S(g) + H_2(g)$	1
		T	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	$^1/_2$
		T	700	$3S + 2H_2O(g) \rightarrow 2H_2S(g) + SO_2(g)$	$^1/_2$
		T	25	$3SO_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(a) + S$	$^1/_2$
		T	25	$S(g) + O_2(g) \rightarrow SO_2(g)$	
23	US -Chlorine [15]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	$^1/_2$
		T	200	$2CuCl + 2HCl \rightarrow 2CuCl_2 + H_2(g)$	1
		T	500	$2CuCl_2 \rightarrow 2CuCl + Cl_2(g)$	1
24	Ispra Mark 9 [13]	T	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	$^3/_2$
		T	150	$3Cl_2(g) + 2Fe_3O_4 + 12HCl \rightarrow 6FeCl_3 + 6H_2O + O_2(g)$	$^1/_2$
		T	650	$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2(g)$	1
25	Ispra Mark 6C [13]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	$^1/_2$
		T	170	$2CrCl_2 + 2HCl \rightarrow 2CrCl_3 + H_2(g)$	1
		T	700	$2CrCl_3 + 2FeCl_2 \rightarrow 2CrCl_2 + 2FeCl_3$	1
		T	500	$2CuCl_2 \rightarrow 2CuCl + Cl_2(g)$	1
		T	300	$CuCl + FeCl_3 \rightarrow CuCl_2 + FeCl_2$	1

*T = thermochemical, E = electrochemical.

†Reactions are stored in database with minimum integer coefficients. Multiplier from reaction junction table converts the results to the basis of one mole of water decomposed.

8. SECOND STAGE SCREENING

The goal of the second stage screening was to reduce the number of cycles under consideration to three or less. Detailed investigations were made into the viability of each cycle. The most recent papers were obtained for each cycle and, when not available from the literature, preliminary block-flow diagrams were made to help gain an understanding of the process complexity. Thermodynamic calculations were made for each chemical reaction over a wide temperature range using HSC Chemistry 4.0 [11]. Each chemical species was considered in each of its potential forms: gas, liquid, solid, and aqueous solution. Each of the principal investigators took responsibility for a part of the investigation and the results were shared.

Once all the background work was completed, the final selection was relatively easy. The three principal investigators independently rated the viability of each cycle. The 25 cycles were considered without reference to their original score and re-rated. Each principal investigator independently assigned a score to each cycle based on their rating of the cycle to be favorable (+1), acceptable (0), or unfavorable (–1). The scores of the three principal investigators were summed, Table 7, and two cycles stood out from all the others with a score of +3. The most highly rated cycles are the adiabatic version of the UT-3 cycle and the sulfur-iodine cycle.

After completing the rating, the rankings were discussed. The rational for the scoring of each cycle is given in Appendix A. Cycles tended to be down-rated for the for the following reasons:

1. If any reaction has a large positive Gibbs free energy, that can not be performed electrochemically nor shifted by pressure or concentration.
2. If it requires the flow of solids.
3. If it is excessively complex.
4. If it can not be well matched to the characteristics of a high temperature reactor.
5. If it required an electrochemical step.

The last two considerations are not as obvious as the others and require additional explanation.

TABLE 7
SECOND STAGE SCREENING SCORES

Cycle	Name	SNL	UK	GA	Score
1	Westinghouse [12]	1	0	0	1
2	Ispra Mark 13 [13]	0	0	0	0
3	UT-3 Univ. of Tokyo [8]	1	1	1	3
4	Sulfur-Iodine [14]	1	1	1	3
5	Julich Center EOS [15]	1	-1	-1	-1
6	Tokyo Inst. Tech. Ferrite [16]	-1	0	0	-1
7	Hallett Air Products 1965 [15]	1	-1	0	0
8	Gaz de France [15]	-1	-1	-1	-3
9	Nickel Ferrite [17]	-1	0	0	-1
10	Aachen Univ Julich 1972 [15]	0	-1	0	-1
11	Ispra Mark 1C [13]	-1	-1	-1	-3
12	LASL- U [15]	1	-1	-1	-1
13	Ispra Mark 8 [13]	0	-1	-1	-2
14	Ispra Mark 6 [13]	-1	-1	-1	-3
15	Ispra Mark 4 [13]	0	-1	-1	-2
16	Ispra Mark 3 [13]	0	-1	-1	-2
17	Ispra Mark 2 (1972) [13]	1	-1	-1	-1
18	Ispra CO/Mn_3O_4 [18]	-1	0	0	-1
19	Ispra Mark 7B [13]	-1	-1	-1	-3
20	Vanadium Chloride [19]	0	1	-1	0
21	Mark 7A [13]	-1	-1	-1	-3
22	GA Cycle 23 [20]	-1	-1	0	-2
23	US -Chlorine [15]	0	1	-1	0
24	Ispra Mark 9 [13]	0	-1	-1	-2
25	Ispra Mark 6C [13]	-1	-1	-1	-3

The nuclear reactor to be used has not been defined except to the point that it will be a high temperature reactor. The coolant may be gas or liquid metal but it is unlikely that it will be water. Certainly, the chemical process will be isolated from the reactor coolant by an intermediate heat transfer loop. The flow rates of the intermediate heat transfer fluid and the reactor coolant will be excessive unless the intermediate heat transfer fluid is operated over a reasonably large temperature range. Thus, a cycle will be well matched to a reactor if it requires energy over a wide temperature range. Figure 15 shows temperature-enthalpy (T-H) curves for three processes matched to the same reactor coolant T-H curve and the same minimum approach temperature. A T-H curve shows the temperature

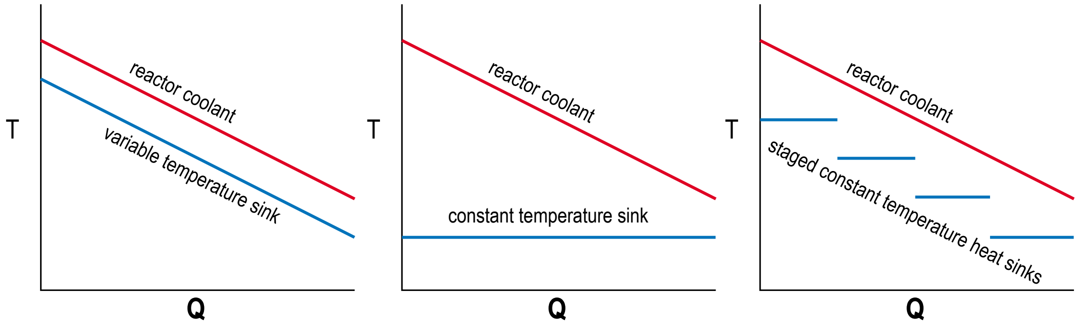


Fig. 15. Matching of thermochemical cycle to reactor.

of the coolant or the process as a function of the amount of heat transferred. As shown, the coolant and process are effectively in counter-current flow heat exchange. In each case, the temperature of the intermediate coolant loop (not shown) is between the reactor temperature and the process temperature.

The first process is well matched as the temperature-enthalpy curves of the process and reactor coolant are parallel. Since the coolant enthalpy is in the form of sensible heat (heat capacity), its temperature enthalpy curve is sloped and approximately linear. For a chemical reaction to have a sloped T-H curve, the reaction equilibria must shift with temperature: the reactants and products are in equilibria over the temperature range but as heat is input to the endothermic chemical reaction the concentration of reactants decreases and products increases. This is the type of T-H curve expected from homogeneous chemical reactions. It will also typify the sensible heat effects of heating or cooling of reactants and products.

The second process is poorly matched. The T-H curve for the process is horizontal, as typified by solid-solid chemical reaction or latent heat effects of phase changes of reactants or products. The third set of curves shows that the matching of processes with horizontal T-H curves can be improved if there is a way to break the process into horizontal segments that require heat at different temperatures. Examples of this would be to employ a number of chemical reactions that occur at different temperatures, or more reasonably, to perform latent heat operations (boiling) at different pressures and therefore at different temperatures.

Hybrid cycles have always attracted considerable interest in that they typically are simpler than pure thermochemical cycles. Never-the-less, they have one characteristic that renders them uneconomic at the scale required for hydrogen production using a nuclear heat source. Energy efficient electrochemical processes require parallel electrodes, small gaps between electrodes and minimal mixing of the anodic and cathodic products — in short they require thin membranes between the anode and cathode. This basically limits efficient electrochemical processes to the small electrode areas that are consistent with thin membrane manufacture. This is not to say that there are not commercial electrochemical process but rather, that the commercial processes are efficient in an economic sense because they make valuable products and not that they are efficient in a thermodynamic sense.

9. SECOND STAGE SHORT LIST

Two cycles were rated far above the others in the second stage screening, the Adiabatic UT-3 and sulfur-iodine cycles.

Adiabatic UT-3 Cycle. The basic UT-3 cycle was first described at University of Tokyo in the late 1970s and essentially all work on the cycle has been performed in Japan. Work has continued to this date with the latest publication last year. Over time the flowsheet has undergone several revisions the most recent, based on the adiabatic implementation of the cycle, was published in 1996. A simplified flow diagram of the Adiabatic UT-3 cycle matched to a nuclear reactor is shown in Fig. 16. The four chemical reactions take place in four adiabatic fixed packed bed chemical reactors that contain the solid reactants and products. The chemical reactors occur in pairs, one pair contains the calcium compounds and the other pair the iron compounds. The nuclear reactor transfers heat through a secondary heat exchanger into the gas stream which traverses through the four chemical reactors, three process heat exchangers, two membrane separators and the recycle compressor in sequence before the gases are recycled to the reactor secondary heat exchanger.

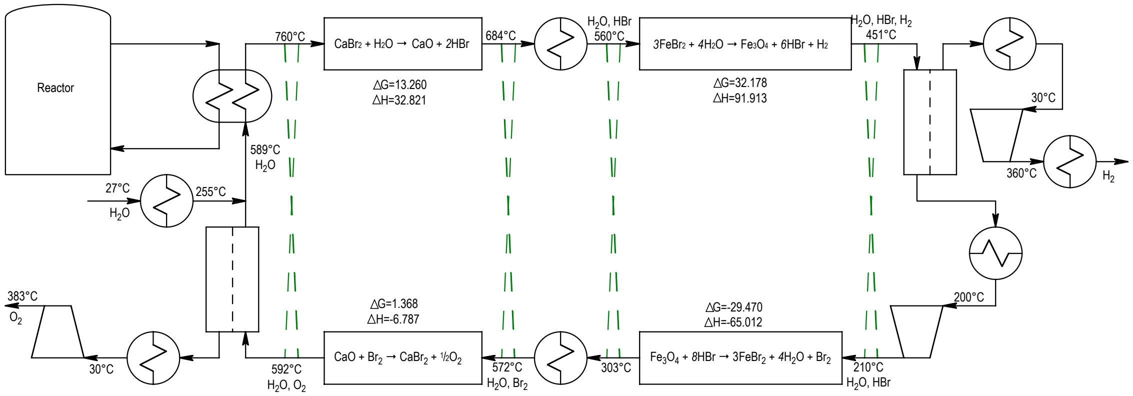


Fig. 16. Adiabatic UT-3 process flow diagram.

At each chemical reactor, the gaseous reactant passes through the bed of solid product until it reaches the reaction front where it is consumed creating gaseous product and solid product. The gaseous product traverses through the unreacted solid and exits the chemical reactor. After some time, perhaps an hour, the reaction front has traveled from near the entrance of the reactor to near the exit. At this point, the flow paths are switched and chemical reactors, in each pair, switch functions. The direction of flow through the reactor also switches so that the reaction front reverses direction and travels back toward the end that had previously been the entrance. The direction must be switched before the reaction front reaches the end of a reactor to prevent large temperature swings but it is desirable for the reaction front to approach the ends of the reactor to reduce the frequency of flow switching.

The gas stream is conditioned, either heated or cooled, before entering the chemical reactor. Since the gaseous reactant/product cannot carry sufficient heat to accomplish the reaction, a large quantity of inert material (steam) comprises the majority of the stream. The total stream pressure is 20 atmospheres and the minimum steam pressure is 18.5 atmospheres. The inert flow provides the additional function of sweeping the products away from the reaction front and thus shifting the reaction equilibrium towards completion. This is necessary since the Gibbs free energy is positive for some of the reactions.

The operation of the semipermeable membranes is somewhat more involved than shown. The partial pressure of hydrogen and oxygen are 0.2 and 0.1 atmospheres respectively. Each gas must be substantially removed from its stream so counter-current operation of the permeator is necessary. This is accomplished by flowing steam past the back side of the membrane. The steam is condensed and separated from the product gas before the product gas is compressed.

The efficiency of hydrogen generation, for a stand-alone plant, is predicted to be 36%–40%, depending upon the efficiency of the membrane separation processes. Higher overall efficiencies, 45%–49%, are predicted for a plant that co-generates both hydrogen and electricity. It is not evident from the published reports if these numbers are based on steady operation or if they take into account the additional inefficiencies associated with the transient operation which occurs when the flow paths are switched.

The chemistry of the cycle has been studied extensively. The basic thermodynamics are well documented. The overall cycle has been demonstrated first at the bench scale and finally in a pilot plant. The UT-3 cycle is the closest to commercial development of any cycle.

The major areas of ongoing research are in the stability of the solids and in the membrane separation processes. For the process to work, the solids must be chemically available to gas phase reactions yet physically stable while undergoing repeated cycling between the oxide and bromide forms. A considerable effort has gone into supporting the reactive solids in a form where they will not be transported by the gas flow. Membranes are being developed which are permeable to oxygen or hydrogen while not being permeable to hydrogen bromide or bromine. There still remains the problem of developing the membrane materials into a physical form that is suitable to large scale economics.

The other questions that require analysis prior to full scale development have to do with the non-steady state operation of the cycle. The non-steady state operation will certainly affect hydrogen production efficiency. Of more concern is the effect of a non-steady-state heat requirement on the reactor operation. This is not expected to be a serious problem as, for large scale hydrogen production, the process will require several completely parallel process modules which can be operated such that, at any time, only a fraction of the chemical plant will be operating in a transient mode.

Overall, the process is in excellent shape for commercial exploitation. There is limited potential for future process improvements as the adiabatic implementation is already quite simple, as thermochemical processes go. There is little room for future efficiency improvements as the process is already operating at the physical limits of its constituents. The maximum $CaBr_2$ operating temperature is already slightly above the melting point. Any attempt to increase efficiency by increasing process temperature will result in migration of the $CaBr_2$.

Sulfur-Iodine Cycle. The sulfur-iodine cycle was first described in the mid 1970s. It was rejected by early workers due to difficulties encountered separating the hydrogen iodide and sulfuric acid produced in Reaction (3). Attempts to use distillation were futile as sulfuric acid and hydrogen iodide react according to the reverse of Reaction (3) when their mixture is heated. The key to successful implementation of the cycle was the recognition that using an excess of molten iodine would result in a two-phase solution, a light phase containing sulfuric acid and a heavy phase containing hydrogen iodide and iodine. Figure 17 shows a block flow diagram of the cycle based on this separation. The sulfur-iodine cycle has been studied by several investigators and while the process as a whole is well defined, there is some uncertainty about the best way of accomplishing the hydrogen iodide decomposition step.

All the early work on the cycle assumed it was necessary to separate the hydrogen iodide from the iodine and water of the heavy phase before performing Reaction (4) to generate hydrogen. Bench scale experiments were made of the total process and the process was matched to a high-temperature nuclear reactor in 1978 and 1980. The latter flowsheet, which was optimized for maximum efficiency, indicated that hydrogen could be produced at 52% efficiency. This is the highest efficiency reported for any water-splitting process, based on an integrated flowsheet.

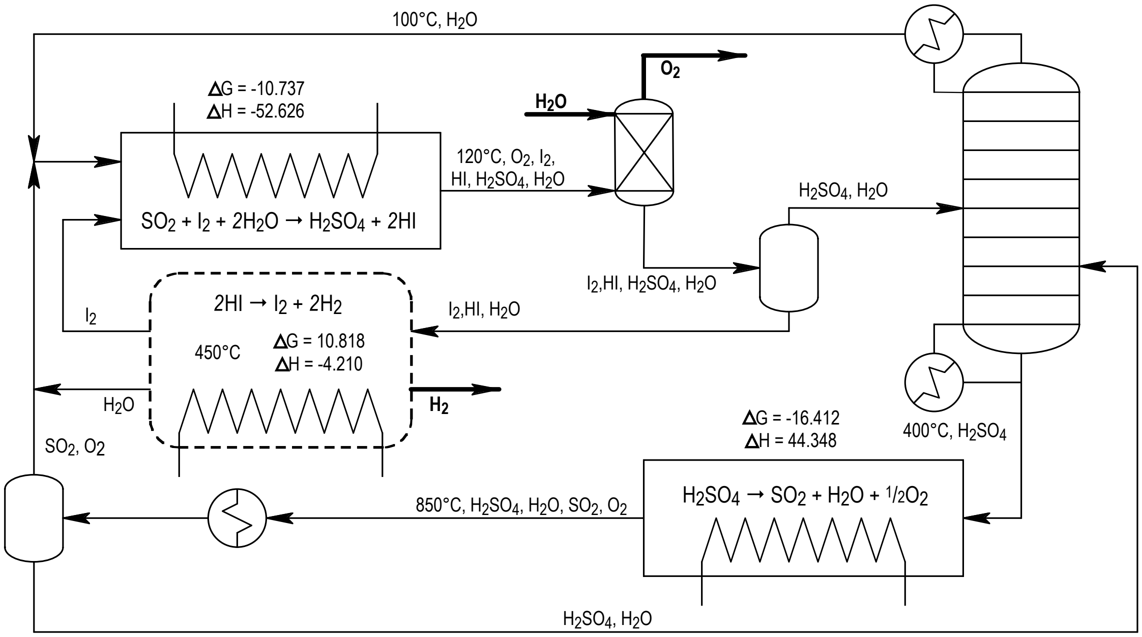


Fig. 17. Sulfur-iodine cycle process flow diagram.

Subsequent to the cessation of development of the sulfur-iodine process in the US, other workers have made several attempts to improve the efficiency of the cycle by modifying the hydrogen production section of the cycle. In particular, researchers at the University of Aachen demonstrated experimentally, that the hydrogen iodide need not be separated from iodine before the decomposition step. Based on their work, they predicted significant increases in efficiency and a 40% decrease in the cost of hydrogen compared with the standard flowsheet. The cost decreases not only because the efficiency increased, but also because the capital intensive heavy phase separation was eliminated. These proposed improvements have never been incorporated into an integrated flowsheet of the sulfur-iodine hydrogen process with a nuclear reactor.

The sulfur-iodine cycle should be matched to a nuclear reactor, incorporating the latest information and thinking. It is the cycle that is almost always used as the standard of comparison as to what can be done with a thermochemical cycle. It was the cycle chosen by LLNL in their conceptual design of a plant to produce synthetic fuels from fusion energy. The Japanese consider the sulfur-iodine cycle to be a back-up for the UT-3 cycle and continue chemical investigations, although they have not published any flowsheets matching the cycle to a nuclear reactor. The cycle has never been matched to a nuclear reactor considering co-generation of electricity. The Japanese found that co-generation gave a 10% efficiency improvement (40% to 50%) for the Adiabatic UT-3 process. If similar improvements are found with the sulfur-iodine cycle, and considering the improvements projected by the University of Aachen, the sulfur-iodine cycle could co-produce hydrogen and electricity at over 60% efficiency.

10. PLANS FOR PHASE 2 AND 3

The sulfur-iodine cycle remains the cycle with the highest reported efficiency, based on an integrated flowsheet. Various researchers have pointed out improvements that should increase the already excellent efficiency of this cycle and, in addition, lower the capital cost significantly. In Phases 2 and 3 we will investigate the improvements that have been proposed to the sulfur-iodine cycle and generate an integrated flowsheet describing a thermochemical hydrogen production plant powered by a high-temperature nuclear reactor. The detailed flowsheet will allow us to size the process equipment and calculate the hydrogen production efficiency. We will finish by calculating the capital cost of the equipment and estimate the cost of the hydrogen produced as a function of nuclear power costs. The scope of work and schedule remain as originally proposed, see Table 8 and Fig. 1.

Phase 2 begins with a detailed process evaluation and a specification of the nuclear reactor thermal interface. The emphasis of Task 2.1, “Detailed Process Evaluation,” will be upon the various methods of accomplishing the hydrogen iodide decomposition step as the down selection to one process has already been accomplished. The reactor will be specified (Task 2.2) only to the degree necessary to define the thermal characteristics of the stream(s) powering the thermochemical process.

The preliminary engineering design of the process (Task 2.3) defines the connectivity of the chemical flowsheet. Each piece of process equipment is indicated and each flowstream is specified as to chemical constituents and an initial estimate of composition, temperature and pressure. Where heating or cooling is indicated, appropriate streams will be paired in heat exchangers. Included in the pairing will be the heat input from the reactor coolant and waste heat to the cooling water flows as well as process-to-process recuperative pairings.

The major effort of Phase 2 will be in developing the material and energy balances for the process (Task 2.4). A chemical process simulator (e.g. AspenPlus) will be the primary tool used in this effort. The full process will be simulated and the flowsheet optimized, in so far as possible, to minimize hydrogen product cost. A process simulator can automatically optimized the process flowsheet to mimimize a specified cost function, but only for a given specification of process connectivity. The process connectivity will be modified progressively and the flowsheet re-optimized as time and funding permit.

TABLE 8
TASKS FOR ALL THREE PHASES

Task Number	Task Description
1.1	Literature survey of new processes
1.2	Develop screening criteria
1.3	Carry out first round screening
1.4	Short report on conclusions
1.5	Carry Out Second Round Screening
1.6	Write Phase 1 report
2.1	Carry out detailed evaluation of few processes to select one
2.2	Define reactor thermal interface
2.3	Preliminary engineering design of selected process
2.4	Develop flowsheet
2.5	Conceptual equipment specifications
2.6	Write Phase 2 Report
3.1	Develop concepts for auxiliary systems
3.2	Refine flowsheet
3.3	Size/cost process equipment
3.4	Evaluate process status
3.5	Write Final Report

As portions of the process design mature, we will define equipment specifications for the chemical process equipment (Task 2.5). These specifications will form the basis for the cost estimates to be made in Phase 3.

The result of Phase 3 will be an evaluation of the process and an estimate of the cost of hydrogen. A key to minimizing the hydrogen cost is to maximize the efficiency of energy utilization. Task 3.1, “Develop auxiliary system concepts,” will investigate the effects of power bottoming and power topping systems. These are the areas in which the Adiabatic UT-3 Process was able to significantly increase the overall efficiency of hydrogen plus electricity co-generation. Meanwhile, the effort of flowsheet optimization will continue (Task 3.2) with an emphasis on incorporating the auxiliary systems.

The key components in estimating the hydrogen production costs are the capital costs of the chemical plant and the nuclear power costs. The capital equipment costs will be estimated using standard chemical engineering techniques based on process equipment sizes and materials (Task 3.3). All the information necessary to specify the process equipment, to this level of detail, will be available from the optimized mass and energy balance. Since the cost of the advanced nuclear reactor will not be available, the cost of hydrogen will be estimated as function of nuclear power costs.

Finally, the overall status of the process will be evaluated (Task 3.4). During the course of this investigation we will have evaluated all the available data on the cycle and its chemistry. We will be able to recommend the steps necessary to bring the process to the point of commercialization.

It would be advantageous, but not essential, if some form of joint collaboration can be established with the Japanese. In particular, we would like access to their latest experimental results on the chemistry of the sulfur-iodine cycle. Although we are concentrating our effort on the sulfur-iodine cycle, we retain our interest in the UT-3 cycle. The work we have proposed, and which we will carry out for the sulfur-iodine cycle has, to a large part, already been performed in Japan for the Adiabatic UT-3 process. We would encourage the Japanese to perform the required non-steady state analysis. After the Japanese and we have completed our respective tasks, we will have two processes from which to select a means of producing hydrogen using nuclear power.

REFERENCES

[1] International Energy Outlook 2000: DOE/EIA-0484(2000)], The Energy Information Administration of the Department of Energy (www.eia.doe.gov).

[2] Annual Energy Outlook 2000 with projections to 2020: DOE/EIA-0383(2000), The Energy Information Administration of the Department of Energy (www.eia.doe.gov).

[3] Analysis of the Impacts of an Early Start for Compliance with the Kyoto Protocol: SR/OIAF/99-02, The Energy Information Administration of the Department of Energy (www.eia.doe.gov).

[4] Impacts of the Kyoto Protocol on U.S. Energy Markets and Economic Activity: SR/OIAF/98-03, The Energy Information Administration of the Department of Energy (www.eia.doe.gov).

[5] EndNote 3.1.2, ISI Research Soft, Berkeley, California (1999). (www.endnote.com).

[6] DOE PubSCIENCE database (www.osti.gov/pubsci).

[7] The IBM Patent Server (www.ibm.com/patent).

[8] Funk, J.K., R.M. Reinstrom, "Energy requirements in the production of hydrogen from water," Ind. Eng. Chem. Proc. Des. Develop. **5**, 336 (1966).

[9] Yalcin, S., "A review of nuclear hydrogen production," Int. J. Hydrogen Energy **14**, 551 (1989).

[10] Yoshida, K., H. Kameyama, et al., "A simulation study of the UT-3 thermochemical hydrogen production process," Int. J. Hydrogen Energy **15,** 171 (1990).

[11] HSC Chemistry 4.0, Outokumpu research Oy, Pori, Finland (1999).

[12] Brecher, L.E., S. Spewock, et al., "Westinghouse sulfur cycle for the thermochemical decomposition of water," Int. J. Hydrogen Energy **21**, 7 (1977).

[13] Beghi, G.E., "A decade of research on thermochemical hydrogen at the joint research center, Ispra," Int. J. Hydrogen Energy **11**, 761 (1986).

[14] Besenbruch, G.E., "General Atomic sulfur-iodine thermochemical water-splitting process," Am. Chem. Soc., Div. Pet. Chem., Prepr. 271, 48 (1982).

[15] Williams, L.O., *Hydrogen Power*, Pergamon Press (1980).

[16] Ueda, R., H. Tagawa, et al., "Production of hydrogen from water using nuclear energy," A review, Japan At. Energy Res. Inst., Tokyo, Japan. (1974) 69.

[17] Tamaura, Y., A. Steinfeld, et al., “Production of solar hydrogen by a novel, 2-step, water-splitting thermochemical cycle,” Energy (Oxford) **20**, 325 (1995).

[18] Bamberger, C.E., “Hydrogen production from water by thermochemical cycles; a 1977 update,” Cryogenics **18**, 170 (1978).

[19] Knoche, K.F. and P. Schuster, “Thermochemical production of hydrogen by a vanadium/chlorine cycle. Part 1: An energy and exergy analysis of the process,” Int. J. Hydrogen Energy **9**, 457 (1984).

[20] Russell, J., Porter, J., “Production of hydrogen from water,” General Atomics Report GA–A12889 (1974).

ACKNOWLEDGMENTS

This work was performed as a collaborative effort between General Atomics, the University of Kentucky and Sandia National Laboratories. Work at General Atomics and the University of Kentucky was supported by the Department of Energy under Nuclear Energy Research Initiative (NERI) Grant No. DE-FG03-99SF21888.

APPENDIX A: COMMENTS ON SCORING OF EACH CYCLE

Cycle 1 — Westinghouse, also Known as the Hybrid Sulfur, GA-22 or Ispra Mark 11 Cycle [12]

(2) $H_2SO_4(g) \rightarrow SO_2(g) + H_2O(g) + {}^1/_2O_2(g)$ (850°C)

(9) $SO_2(aq) + 2H_2O(\ell) \rightarrow H_2SO_4(aq) + H_2(g)$ (80°C electrolysis)

Advantages. This cycle is an all fluid process. There are only two reactions. The high temperature step (2), is actually a sequence of Reactions (2a) and (2b) that accept heat over a reasonably large temperature range and thus can be well matched to the sensible heat of a reactor coolant. The thermodynamic properties of the chemical species are well known. Side reactions are minimal. The cycle has been fully flow-sheeted. The cycle was operated at bench scale by Westinghouse and at the CRISTINA demonstration pilot plant scale by The Commission of the European Communities at their Ispra Research Establishment. The sulfuric acid decomposition step was also demonstrated using concentrated solar energy on a solar power tower.

Disadvantages. This cycle is a hybrid cycle and as such retains the scale-up problems inherent in electrochemical processes. Electrochemical process are limited by the surface area of the electrodes and can only be scaled-up, after the maximum practical electrode area is reached, by adding modules.

Comments. The cycle has been studied extensively by both Westinghouse and Ispra. The cycle was used by Ispra as part of the CRISTINA demonstration of sulfuric acid cracking step of the Mark 13 Cycle. Although not deemed as efficient as Mark 13 by Ispra, it was easier to use in the demonstration. There is probably little room for improvement since the last Westinghouse flowsheet.

Cycle 2 — Ispra Mark 13 [13]

(2) $H_2SO_4(g) \rightarrow SO_2(g) + H_2O(g) + {}^1/_2O_2(g)$ (850°C)

(10) $Br_2(aq) + SO_2(aq) + 2H_2O(\ell) \rightarrow 2HBr(g) + H_2SO_4(aq)$ (77°C)

(11) $2HBr(g) \rightarrow Br_2(\ell) + H_2(g)$ (77°C electrolysis)

Advantages. This cycle is an all fluid process. There are only three reactions. The high temperature step (2), is actually a sequence of Reactions (2a) and (2b) that adsorb heat over a reasonably large temperature range and thus can be well matched to the sensible heat of a reactor coolant. The thermodynamic properties of the chemical species are well known. Side reactions are minimal. The cycle has been fully flow-sheeted. The cycle was operated at the pilot plant scale by The Commission of the European Communities at their Ispra Research Establishment. The sulfuric acid decomposition step was also demonstrated using concentrated solar energy on a solar power tower. The electrolysis step has been operated at the pilot plant scale as part of a SO_2 recovery process at an oil refinery on Sardinia.

Disadvantages. This cycle is a hybrid cycle and as such retains the scale-up problems inherent in electrochemical processes. The electrode systems developed at Ispra for this cycle appear to be very difficult to scale-up.

Comments. The cycle has been extremely well studied and there is seems to be little room for improvement over the last CEC-Ispra designs.

Cycle 3 — University of Tokyo 3 (UT-3) [8]

(5) $2Br_2(g) + 2CaO(s) \rightarrow 2CaBr_2(s) + {}^1/_2O_2(g)$ (672°C)

(6) $3FeBr_2(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 6HBr(g) + H_2(g)$ (560°C)

(7) $CaBr_2(s) + H_2O(g) \rightarrow CaO(s) + 2HBr(g)$ (760°C)

(8) $Fe_3O_4(s) + 8HBr(g) \rightarrow Br_2(g) + 3FeBr_2(s) + 4H_2O(g)$ (210°C)

Advantages. Although this cycle is based on solids, the solid materials remain in fixed beds and only gasses are transported. The cycle has been fully flow-sheeted. The reported efficiency is 40% in the adiabatic bed implementation. Efficiencies as high as 50% are claimed for a plant that co-produces hydrogen and electricity. The cycle has been operated at the pilot plant scale.

Disadvantages. The process involves solids. The cycle cannot be operated in steady-state mode without moving solids. Beds of solid material must be periodically transitioned from one temperature to another. The high temperature endothermic steps are operated under conditions in which the free energy of the reaction is positive. These reactions are forced to proceed by sweeping the reaction products out of the reaction zone. These reactions are operated very near the melting point of the bromides and, if melting occurs, transport of the molten bromides could lead to blockage of the beds.

Comments. This cycle has been extensively studied in Japan. It is the only cycle presently being studied at large scale. There appear to be some parts of this reaction that are not discussed in the open literature, indicating that there may be some surprises that make this cycle more favorable than it appears. The reaction which consumes $CaBr_2$ is said to occur at 750°C but at this temperature $CaBr_2$ is liquid.

Cycle 4 — Sulfur-Iodine, Also Known as the Iodine-Sulfur, General Atomic or Ispra Mark 16 Cycle [14]

(2) $H_2SO_4(g) \rightarrow SO_2(g) + H_2O(g) + {}^1/_2O_2(g)$ (850°C)

(3) $I_2(\ell_2) + SO_2(aq) + 2H_2O(\ell_2) \rightarrow 2HI(\ell) + H_2SO_4(aq)$ (120°C)

(4) $2HI(\ell) \rightarrow I_2(\ell) + H_2(g)$ (450°C)

Advantages. This cycle is an all fluid process. The high temperature step (2), is actually a sequence of Reactions (2a) and (2b) that adsorb heat over a reasonably large temperature range and thus can be well matched to the sensible heat of a reactor coolant. The thermodynamic properties of the chemical species are well known. Side reactions are minimal. The cycle has been fully flow sheeted. The cycle has been operated at the bench scale in the US and portions of it have been operated at bench scale in Japan. The sulfuric acid decomposition step was operated at the bench scale by General Atomics. This process has the highest quoted efficiency (52%) of any process that has been fully flow sheeted. The sulfuric acid decomposition step was also demonstrated using concentrated solar energy on a solar power tower. This cycle is unique in that the hydrogen is generated at high pressure (50 atmospheres) eliminating the necessity of compressing the hydrogen for pipeline transmission or other downstream processing. Compression of hydrogen is quite energy intensive and is to be avoided if possible.

Disadvantages. Separation of the dense liquid phase from the acid generating reaction into HI and I_2 is accomplished by extracting water into concentrated phosphoric acid in the standard flowsheet. There is a significant amount of water in the phase and the phosphoric acid is only effective at concentrations above 85% so there is a large recycle of phosphoric acid through the phosphoric acid dehydration system. The phosphoric acid dehydration system is thermodynamically efficient, but is capital intensive.

Comments. This cycle has been studied extensively by GA and more recently by other researchers. It was called Mark 16 by the researchers at Ispra. Much of the study by other researchers has concentrated on the separation of HI and I_2 and several of the proposed alternative schemes look promising. Unfortunately, none of the alternative schemes have been integrated into a complete flowsheet so the integrated effect of the improved schemes cannot be ascertained.

Cycle 5 — Julich Center EOS [15]

(12) $Fe_3O_4(s) + 3FeSO_4(s) \rightarrow 3Fe_2O_3(s) + 3SO_2(g) + {}^1/_2O_2(g)$ 800°C

(13) $3Fe_2O_3(s) + 3SO_2(g) \rightarrow 3FeO(s) + 3FeSO_4$ 200°C

(14) $3FeO(s) + H_2O(g) \rightarrow Fe_3O_4(s) + H_2(g)$ 700°C

Advantages. There are only three reactions and the high temperature reaction occurs at a reasonable temperature.

Disadvantages. This process involves moving and separating solids. There does not appear to be any way to implement the process without moving solids. The solid-solid Reaction (12) between Fe_3O_4 and $FeSO_4$ probably requires a fluxing agent unless the two solids are finely ground together or occur in the same crystal. They could only occur in the same crystal if they are both present in the third Reaction (14), but it is not possible for hydrogen to be released in the presence of sulfate at 700°C without reducing the sulfate to SO_2. This means the FeO + $FeSO_4$ must be physically separated. The SO_2 and O_2 must be separated hot to keep from generating SO_3 while cooling.

Comments. May be able to separate and recombine solids with aqueous steps. This has severe negative impacts on the overall efficiency. This is one of the only $FeCl_x$ cycles that made it through our first cut that does not appear to have a high sensitivity to O_2 carry through.

Cycle 6 — Manganese Ferrite or Tokyo Institute of Technology Ferrite [16]

(15) $2MnFe_2O_4(s) + 3Na_2CO_3(\ell) + H_2O(s) \rightarrow$
$2\ Na_3MnFe_2O_6(s) + 3CO_2(g) + H_2\ (g)$ 1000°C

(16) $2Na_3MnFe_2O6(s) + 3CO_2\ (g) \rightarrow$
$2MnFe_2O_4(s) + 3Na_2CO_3(s) + {}^1/_2O_2\ (g)$ 600°C

Advantages. There are 2 reactions. The reactions involve solids but they don’t need to move.

Disadvantages. The process involves solids. Experimental results indicate that there is only 5% conversion per pass. Thermodynamic data are unavailable for the ferrites as pure phases, let alone as the solid solutions. Solid solutions must be important as the reaction does not form a new sold phase. If a new solid phase were formed, the reaction would proced to completion. The H_2 and CO_2 products will equilibrate to also form CO and H_2O. Sodium carbonate is molten in the high temperature Reaction (15) and could separate before reacting. The highest temperature required is higher than desired.

Comments. This is from class of cycles which could be interesting if the reactions proceeded to a significant extent. Such a small change in a large molecule indicates that the ΔG will not be largely influenced by ΔS. Overall efficiency in terms of thermal input is likely to be very low due to cycling of solid bed between temperatures.

Cycle 7 — Hallett Air Products 1965 [15]

(17) $Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + {}^1/_2O_2(g)$ 850°C

(18) $2HCl(aq) \rightarrow Cl_2(g) + H_2(g)$ 25°C electrolysis

Advantages. This cycle is an all fluid process. There are only two chemical reactions and only one element other than hydrogen and oxygen. There is little potential for side reactions.

Disadvantages. This cycle is a hybrid cycle and as such retains the scaling problems inherent in electrochemical processes. Electrochemical process are limited by the surface area of the electrodes and can only be scaled-up, after the maximum practical electrode area is reached, by adding modules. The reversible voltage for the electrolysis of HCl (18) is greater than that for water. ΔG is 62.676 kcal/mole (E_0 = 1.36 volts) for the reactants and products in their standard states as compared with 57.662 kcal/mole (E_0 = 1.25 volts) for water electrolysis. This will give a 10% penalty before any other considerations. In terms of the adiabatic voltage the situation is worse, 1.73 vs. 1.48 volts or a 15% penalty. At elevated temperatures the relative voltage difference improves for the isothermal case and gets worse for the adiabatic case.

Comments. If the HCl concentration was high the electrode voltage would be reduced. There is plenty of heat available so there should be no problem is supplying the heat necessary to operate the cell isothermally. The cycle might compete with electrolysis if the over voltage for chlorine production is low compared with the over voltage for oxygen production.

Cycle 8 — Gaz de France [15]

(19) $2K(\ell) + 2KOH(\ell) \rightarrow 2K_2O(s) + H_2(g)$ 750°C

(20) $2K_2O(s) \rightarrow 2K(\ell) + K_2O_2(\ell)$ 825°C

(21) $K_2O_2(s) + H_2O(g) \rightarrow 2KOH(aq) + {}^1/_2O_2(g)$ 125°C

Advantages. There are only three chemical reactions and only one element other than hydrogen and oxygen.

Disadvantages. The process involves moving solids and solids melting and solidifying. The hydrogen production Reaction (19) is not spontaneous at any temperature.

Comments. The hydrogen producing Reaction (19) might be forced by using a sweep gas or a vacuum to remove the hydrogen and shift the reaction. Recovery of the hydrogen from the vacuum or sweep gas will be energy intensive. There are some safety concerns in dealing with molten K and its oxides.

Cycle 9 — Nickel Ferrite [15]

(22) ${}^1/_2NiMnFe_4O_6(s) + H_2O(g) \rightarrow {}^1/_2NiMnFe_4O_8(s) + H_2(g)$ 800°C

(23) ${}^1/_2NiMnFe_4O_8(s) \rightarrow {}^1/_2NiMnFe_4O_6(s) + {}^1/_2O_2(g)$ 800°C

Advantages. Only two reactions and the solid reactants/products do not move.

Disadvantages. The process involves solids. Experimental work showed only very low conversion. Evacuation or a sweep gas would be require to remove the oxygen.

Comments. This is from class of cycles which could be interesting if the reactions proceeded to a significant extent. Such a small change in a large molecule indicates that the ΔG will not be largely influenced by ΔS. Overall efficiency in terms of thermal input is likely to be very low due to cycling of solid bed between temperatures. Theoretically there can be no cycle if there is no temperature difference between the reactions. There is very little information in the literature on this cycle.

Cycle 10 — Aachen Univ Julich 1972 [15]

(17)	$Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + {}^1/_2O_2(g)$	850°C
(24)	$2CrCl_2(s) + 2HCl(g) \rightarrow 2CrCl_3(s) + H_2(g)$	170°C
(25)	$2CrCl_3(s) \rightarrow 2CrCl_2(s) + Cl_2(g)$	800°C

Advantages. The solids could stay in fixed beds, they do not have to move or be separated. Only three reactions. The temperature range is good.

Disadvantages. The process involves solids. The chlorine production Reaction (25) is not favorable until above 1200°C. The only way to shift the reaction at the indicated temperature is to sweep the chlorine away with an inert gas or use a vacuum. The inert gas would end up mixed with the oxygen and either have to be separated or thrown away.

Comments. If the temperature is actually raised to the required temperature of Reaction (25) the $CrCl_2$ (mp 814°C) is liquid and could easily be separated from the $CrCl_3$. The University of Aachen decided to not continue work on this cycle.

Cycle 11 — Ispra Mark 1C [13]

(26)	$2CuBr_2(aq) + 2Ca(OH)_2(aq) \rightarrow 2CuO(s) + 2CaBr_2(aq) + 2H_2O$	100°C
(27)	$2CuO(s) \rightarrow Cu_2O(s) + {}^1/_2\ O_2(g)$	900°C
(7[*])	$2CaBr_2(s) + 2H_2O(g) \rightarrow 2Ca(OH)_2(s) + 4HBr(g)$	730°C
(28)	$Cu_2O(s) + 4HBr(g) \rightarrow 2CuBr_2 + H_2(g) + H_2O(g)$	100°C

Advantages. Two high temperature reactions may indicated potential for a high efficiency.

Disadvantages. This process involves separating and moving solids. Thermodynamics for $CuBr_2(aq)$ are not well known.

Comments. This cycle was rejected by its initial proponent in favor of Mark 13.

---

[*] Multiple of standard reaction.

Cycle 12 — LASL-U [15]

(29) $3CO_2(g) + U_3O_8(s) + H_2O(\ell) \rightarrow 3UO_2CO_3(aq) + H_2(g)$ 25°C

(30) $3UO_2CO_3(s) \rightarrow 3CO_2(g) + 3UO_3(s)$ 250°C

(31) $3UO_3(s) \rightarrow U_3O_3(s) + {}^{1}/_{2}O_2(g)$ 700°C

Advantages. Only three reactions.

Disadvantages. The process involves moving solids and concentrating salt solutions to dry solids.

Comments. Public perception of a uranium process might be that it was a health hazard. Production of very fine particles of UO_x could be a problem for workers within the plant especially during down-time maintenance.

Cycle 13 — Ispra Mark 8 [13]

(32) $3MnCl_2(s) + 4H_2O(g) \rightarrow Mn_3O_4(s) + 6HCl(g) + H_2(g)$ 700°C

(33) $3MnO_2(s) \rightarrow Mn_3O_4(s) + {}^{1}/_{2}O_2(g)$ 900°C

(34) $6HCl(aq) + {}^{3}/_{2}Mn_3O_4(s) \rightarrow 3MnCl_2(aq) + {}^{3}/_{2}MnO_2(s) + 3H_2O(\ell)$ 100°C

Advantages. Only three reactions.

Disadvantages. The process involves moving solids and concentrating salt solutions to dry solids.

Comments. Manganese has numerous oxidation states/phases and intermediates that could be formed. Care would have to be taken to investigate all side products and be certain that there are no thermodynamic sinks that will form over time. This cycle was rejected by its initial proponent in favor of Mark 13.

Cycle 14 — Ispra Mark 6 [13]

(17) $Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + {}^{1}/_{2}O_2(g)$ 850°C

(24) $2CrCl_2(s) + 2HCl(g) \rightarrow 2CrCl_3(s) + H_2(g)$ 170°C

(35) $2CrCl_3(s) + 2FeCl_2(\ell) \rightarrow 2CrCl_2(s) + 2FeCl_3(g)$ 700°C

(36) $2FeCl_3(g) \rightarrow Cl_2(g) + 2FeCl_2(s)$ 420°C

Advantages. Good temperature match.

Disadvantages. The process involves melting, separating and moving solids. The proponents found experimentally that $FeCl_3$ decomposition and hydrolysis of $FeCl_2$ to iron oxides were critical problems for which no suitable solution could be found.

Comments. Reaction (35) is operated above the melting point of $FeCl_2$(mp 677°C) so that it acts as a flux and increases the reaction rate. This cycle was rejected by its initial proponent in favor of Mark 13.

Cycle 15 — Ispra Mark 4 [13]

(17) $Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + {}^1/_2O_2(g)$ 850°C

(37) $2FeCl_2(aq) + 2HCl(aq) + S(s) \rightarrow 2FeCl_3(aq) + H_2S(g)$ 100°C

(36) $2FeCl_3(g) \rightarrow Cl_2(g) + 2FeCl_2(s)$ 420°C

(38) $H_2S(g) \rightarrow S(g) + H_2(g)$ 800°C

Advantages. Two high temperature reactions may promote high efficiency.

Disadvantages. The process involves separating and moving solids. The proponents found experimentally that $FeCl_3$ decomposition and hydrolysis of $FeCl_2$ to iron oxides were critical problems for which no suitable solution could be found.

Comments. This cycle was rejected by its initial proponent in favor of Mark 13.

Cycle 16 — Ispra Mark 3 [13]

(17) $Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + {}^1/_2O_2(g)$ 850°C

(39) $2VOCl_2(s) + 2HCl(g) \rightarrow 2VOCl_3(g) + H_2(g)$ 170°C

(40) $2VOCl_3(g) \rightarrow Cl_2(g) + 2VOCl_2(s)$ 200°C

Advantages. Only three reactions. The temperature fit is good.

Disadvantages. Reactions (39) and (40) both have positive ΔGs. The equilibria of Reaction (39) can be shifted by purging but the equilibria of Reaction (40) cannot. The process involves moving of solids.

Comments. The boiling point of $VOCl_3$ is 127°C. Operating at lower temperature where $VOCl_3$ is liquid does not help the thermodynamics. This cycle was rejected by its initial proponent in favor of Mark 13.

Cycle 17 — Ispra Mark 2 (1972) [13]

(41) $2Na_2O.MnO_2(s) + 2H_2O(\ell) \rightarrow 4NaOH(aq) + 2MnO_2(s)$ 100°C

(42) $2MnO_2(s) \rightarrow Mn_2O_3(s) + {}^1/_2O_2(g)$ 487°C

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

Advantages. Only three reactions. The upper temperature is a good match to a nuclear reactor.

Disadvantages. The process involves moving solids and concentrating salt solutions to dry solids.

Comments. Caution is required in cycles involving manganese due to the many possible oxidation states. This cycle was rejected by its initial proponent in favor of Mark 13.

Cycle 18 — Ispra CO/Mn_3O_4 [18]

(44) $3Mn_2O_3(s) \rightarrow 2Mn_3O_4(s) + {}^1/_2O_2(g)$ 977°C

(45) $C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$ 700°C

(46) $CO(g) + 2Mn_3O_4(s) \rightarrow C(s) + 3Mn_2O_3(s)$ 700°C

Advantages. Only three reactions. The solids do not need to move.

Disadvantages. The process involves moving and separating solids. The carbon generating Reaction (46) is thermodynamically unfavorable. The reaction could be shifted by raising the pressure but it would require in excess of 10^{13} atmospheres. Carbon would need to be separated from Mn_2O_3.

Comments. Caution is required in cycles involving manganese due to the many possible oxidation states. This cycle was rejected by its initial proponent in favor of Mark 13.

Cycle 19 — Ispra Mark 7B [13]

(47) $^{3}/_{2}Fe_2O_3(s) + {}^{9}/_{2}Cl_2(g) \rightarrow 3FeCl_3(g) + {}^{9}/_{4}O_2(g)$ 1000°C

(48) $3FeCl_3(g) \rightarrow {}^{3}/_{2}Cl_2(g) + 3FeCl_2(s)$ 420°C

(49) $3FeCl_2(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 6HCl(g) + H_2(g)$ 650°C

(50) $Fe_3O_4(s) + 1/4O_2(g) \rightarrow {}^{3}/_{2}Fe_2O_3(s)$ 350°C

(51) $6HCl(g) + {}^{3}/_{2}O_2(g) \rightarrow 3Cl_2(g) + 3H_2O(g)$ 400°C

Advantages. No advantages over other cycles.

Disadvantages. The process involves five reactions. The process involves separating and moving solids. The proponents found experimentally that $FeCl_3$ decomposition and hydrolysis of $FeCl_2$ to iron oxides were critical problems for which no suitable solution could be found. Oxygen must be separated from gaseous ferric chloride at high temperature. The high temperature reaction is not favorable below 1200°C.

Comments. The process involves separating and moving solids. Reaction (47) appears to require 1200°C instead of the 1000°C indicated. The reaction can be shifted by sweeping the gaseous products away with chlorine gas. Reaction (49) requires purging with water to shift the reaction equilibria. This cycle was rejected by its initial proponent in favor of Mark 13.

Cycle 20 — Vanadium Chloride [19]

(17) $Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + {}^{1}/_{2}O_2(g)$ 850°C

(52) $2HCl(g) + 2VCl_2(s) \rightarrow 2VCl_3(s) + H_2(g)$ 25°C

(53) $4VCl_3(s) \rightarrow 2VCl_4(g) + 2VCl_2(s)$ 700°C

(54) $2VCl_4(\ell) \rightarrow Cl_2(g) + 2VCl_3(s)$ 25°C

Advantages. The cycle has a good temperature range. All process chemistry has been demonstrated.

Disadvantages. The process involves solids.

Comments. The $HCl(g)$ and $O_2(g)$ from Reaction (17) should be separated without the use of water as any water left in the HCl would produce VOCl as a byproduct of

Reaction (52). This process would be enhanced by the use of an oxygen permeable membrane. A variation of this process was fully flow-sheeted by the University of Aachen, with a resulting efficiency of 42.5%.

Cycle 21 — Mark 7A [13]

(55)	$3FeCl_3(\ell) \rightarrow {}^{3}/_{2}Cl_2(g) + 3FeCl_2(s)$	420°C
(17)	$Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + {}^{1}/_{2}O_2(g)$	850°C
(49)	$3FeCl_2(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 6HCl(g) + H_2(g)$	650°C
(50)	$Fe_3O_4(s) + 1/4O_2(g) \rightarrow {}^{3}/_{2}Fe_2O_3(s)$	350°C
(51)	${}^{3}/_{2}Cl_2(g) + {}^{1}/_{2}Fe_2O_3(s) \rightarrow FeCl_3(g) + {}^{3}/_{4}O_2(g)$	1000°C
(56)	$Fe_2O_3(s) + 6HCl(aq) \rightarrow 2FeCl_3(aq) + 3H_2O(\ell)$	120°C

Advantages. None compared with other cycles.

Disadvantages. Five chemical reactions. The maximum temperature is higher than desired. The process involves separating and moving solids. The proponents found experimentally that $FeCl_3$ decomposition and hydrolysis of $FeCl_2$ to iron oxides were critical problems for which no suitable solution could be found.

Comments. This cycle was rejected by its initial proponent in favor of Mark 13.

Cycle 22 — GA Cycle 23 [20]

(38)	$H_2S(g) \rightarrow S(g) + H_2(g)$	800°C
(2*)	$3H_2SO_4(g) \rightarrow 3SO_2(g) + 3H_2O(g) + {}^{3}/_{2}O_2(g)$	850°C
(57)	${}^{3}/_{2}S(g) + H_2O(g) \rightarrow H_2S(g) + {}^{1}/_{2}SO_2(g)$	700°C
(58)	${}^{9}/_{2}SO_2(g) + 3H_2O(l) \rightarrow 3H_2SO_4(aq) + {}^{3}/_{2}S(s)$	25°C
(59)	$S(g) + O_2(g) \rightarrow SO_2(g)$	850°C

Advantages. This cycle is an all fluid process.

---

[*] Multiple of standard reaction.

Disadvantages. The kinetics of the sulfur generating reaction may be slow.

Comments. This cycle was rejected by its initial proponent in favor of another cycle. Reactions (59) and (2) can be combined with the sulfur being injected downstream of the heat input to boost the reaction temperature and the conversion of SO_2.

Cycle 23 — US-Chlorine [15]

(17) $Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + {}^1/_2O_2(g)$ 850°C

(60) $2CuCl(s) + 2HCl \rightarrow 2CuCl_2(s) + H_2(g)$ 200°C

(61) $2CuCl_2(s) \rightarrow 2CuCl(\ell) + Cl_2(g)$ 500°C

Advantages. Three reactions. The temperature range is appropriate.

Disadvantages. The process involves solids with phase changes. Reaction (60) has a positive ΔG but the equilibria can be shifted by purging.

Comments. Thermodynamic analysis indicated that Reaction (60) needs to be performed at room temperature.

Cycle 24 — Ispa Mark 9 [115]

(55) $3FeCl_3(\ell) \rightarrow {}^3/_2Cl_2(g) + 3FeCl_2(s)$ 420°C

(62) ${}^3/_2Cl_2(g) + Fe_3O_4 + 6HCl \rightarrow 3FeCl_3 + 3H_2O + {}^1/_2O_2(g)$ 150°C

(49) $3FeCl_2(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 6HCl(g) + H_2(g)$ 650°C

Advantages. Three reactions.

Disadvantages. The process involves separating and moving solids. The proponents found experimentally that $FeCl_3$ decomposition and hydrolysis of $FeCl_2$ to iron oxides were critical problems for which no suitable solution could be found.

Comments. This cycle was rejected by its initial proponent in favor of Mark 13.

Cycle 25 — Ispa Mark 6C [13]

(17) $Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + {}^{1}/_{2}O_2(g)$ 850°C

(24) $2CrCl_2(s) + 2HCl(g) \rightarrow 2CrCl_3(s) + H_2(g)$ 170°C

(35) $2CrCl_3(s) + 2FeCl_2(\ell) \rightarrow 2CrCl_2(s) + 2FeCl_3(g)$ 700°C

(61) $2CuCl_2(s) \rightarrow 2CuCl(\ell) + Cl_2(g)$ 500°C

(63) $CuCl(s) + FeCl_3(s) \rightarrow CuCl_2(s) + FeCl_2(s)$ 300°C

Advantages. None.

Disadvantages. Five chemical reactions. Reaction (63) is a solid-solid reaction that probably requires a flux. The process involves separating and moving solids. The proponents found experimentally that $FeCl_3$ decomposition and hydrolysis of $FeCl_2$ to iron oxides were critical problems for which no suitable solution could be found.

Comments. This cycle was rejected by its initial proponent in favor of Mark 13.