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ABSTRACT

This report describes work accomplished during the first year of a three-year project 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 for further detailed consideration. An exhaustive literature scan was done to locate cycles, which were screened to select two as the most promising candidates: the adiabatic UT-3 cycle and the sulfur-iodine cycle. The UT-3 is being pursued in Japan. During Phases 2 and 3 of this study, we will pursue the sulfur-iodine cycle, developing flowsheets and making preliminary engineering estimates of the size, cost, and efficiency of the plant and of the cost of product hydrogen.

1. INTRODUCTION AND SUMMARY

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.

Currently no large scale, cost-effective, environmentally attractive hydrogen production process is available for commercialization nor has such a process been identified.

Hydrogen produced 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 the goal of a low-polluting transportable energy feedstock.

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 have 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 100 cycles have been proposed, but substantial research has been executed on only a few.

The purpose of the project was 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 from an energy source that has little or no affect on greenhouse gas emissions and whose availability and sources are domestically controlled. This will help to ensure energy supply for 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 and was performed as a collaborative effort between General Atomics (GA), the University of Kentucky (UK) and Sandia National Laboratories (SNL) under the Department of Energy, Nuclear Energy Research Initiative (DOE/NERI) Grant Nos. DE-FG03-99SF21888 (GA/UK) and DE-FG03-99SF0238 (SNL). 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.

An exhaustive literature search was performed to locate all cycles previously proposed. The cycles located were then screened using objective criteria, to determine which can benefit, in terms of efficiency and cost, from the high-temperature capabilities of advanced nuclear reactors. 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, two cycles were selected: the adiabatic 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. The cycle has been studied extensively in Japan by a number of organizations, including Toyo Engineering and JAERI. 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 the assumption of electricity co-generation along with the hydrogen. A significant amount of engineering development work, 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. In addition, various researchers have pointed out improvements that should increase the already high efficiency (52%) of this cycle and 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. We will then size the process equipment, calculate the hydrogen production efficiency, and estimate the cost of the hydrogen produced as a function of nuclear power costs.

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.

2. LITERATURE SEARCH AND SCREENING

2.1. PROJECT DATABASES

An important part of the process identification and 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. An EndNote [5] database was used to maintain the project literature database and a Microsoft™ Access® database was required to keep track of all the thermochemical cycles.

In our approach 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. 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. 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 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. 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 literature database and linked to the cycle database.

2.2. LITERATURE SEARCH

The literature survey was designed to locate substantially all thermochemical water-splitting cycles that have been proposed in the open literature.

Interest in thermochemical water splitting has varied greatly with time. Figure 1 indicates when the references in the database were published. The initial interest in the early 1960s [6] 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 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 [7], 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.

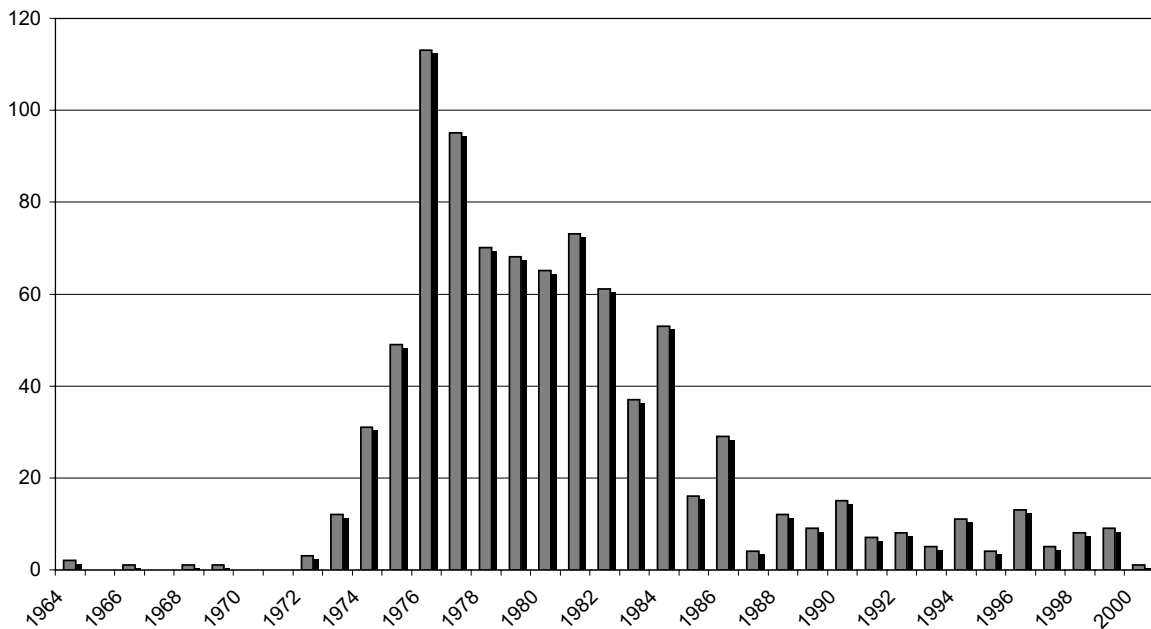


Fig. 1. Publications by year of issue.

2.3. PRELIMINARY SCREENING CRITERIA

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. Table 1 gives the basis for selecting the screening criteria and the metrics chosen.

The translation of each metric to a score based on the metric, is given in Table 2. 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.

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.

2.4. 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

TABLE 1
RATIONALE FOR DEVELOPMENT OF FIRST ROUND SCREENING CRITERIA

Desirable Characteristic	Rationale	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 2
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	8	7	6	5	4	3	2	1	0
3. Number of elements	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, V, Sr	Cu, Zn, Zr, Ni, B, Ba, Li, Br, Cr	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. <i>aqua regia</i>	–	–	–	–	–	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 estimate based on detailed flow sheet	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.

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.

2.5. 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 [8] 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 3, along with their scores. One literature reference is included for each cycle.

2.6. 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 developed 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 [8]. Each chemical species was considered in each of its potential forms: gas, liquid, solid, and aqueous solution. 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

TABLE 3
SHORT LIST OF CYCLES AND THEIR SCORES

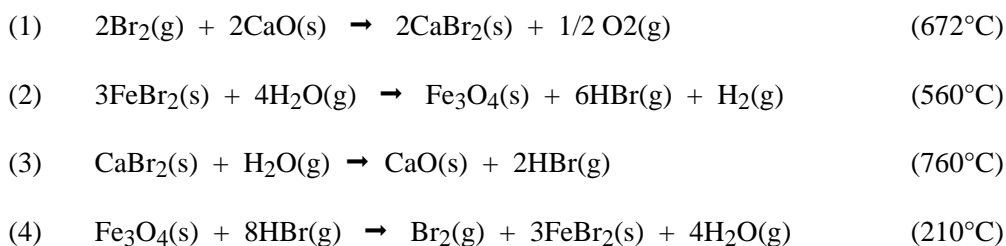
Cycle#	Name	Class	Max T	Elem	#elem	#seps	#Rxn	Seps	Elms	Abund	Corr	Solids	Temp	Pubs	Tests	Data	Total
1	Westinghouse [12]	H	850 S		1	2	10	8	10	9	5	10	9	10	6	8	85
2	Ispra Mark 13 [13]	H	850 Br,S		2	3	9	7	9	7	5	10	9	10	6	8	80
3	UT-3 Univ. of Tokyo [8]	T	750 Br,Ca,Fe		3	3	6	7	8	7	5	6	10	10	10	10	79
4	Sulfur-Iodine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

each cycle based on their rating of the cycle to be favorable (+1), acceptable (0), or unfavorable (−1). Cycles tended to be down-rated for the following reasons:

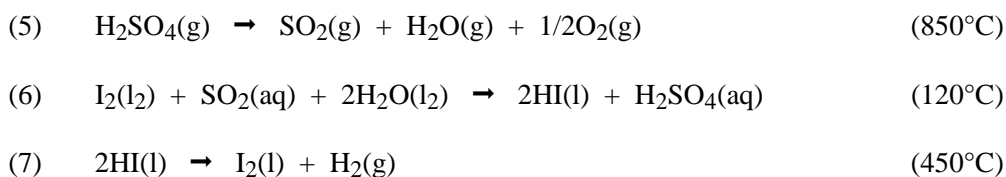
1. If any reaction has a large positive Gibbs-free energy, that cannot be performed electrochemically nor shifted by pressure or concentration.
2. If it requires the flow of solids.
3. If it is excessively complex.
4. If it cannot be well matched to the characteristics of a high temperature reactor.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

The scores of the three principal investigators were summed and are shown in Table 4. Two cycles stood out from all the others with a score of +3. The most highly rated cycles were the adiabatic version of the UT–3 cycle and the sulfur-iodine cycle.

University of Tokyo 3 (UT–3) Cycle [8]



Sulfur-Iodine Cycle



2.6.1. 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. 2. 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.

TABLE 4
SECOND STAGE SCREENING SCORES

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

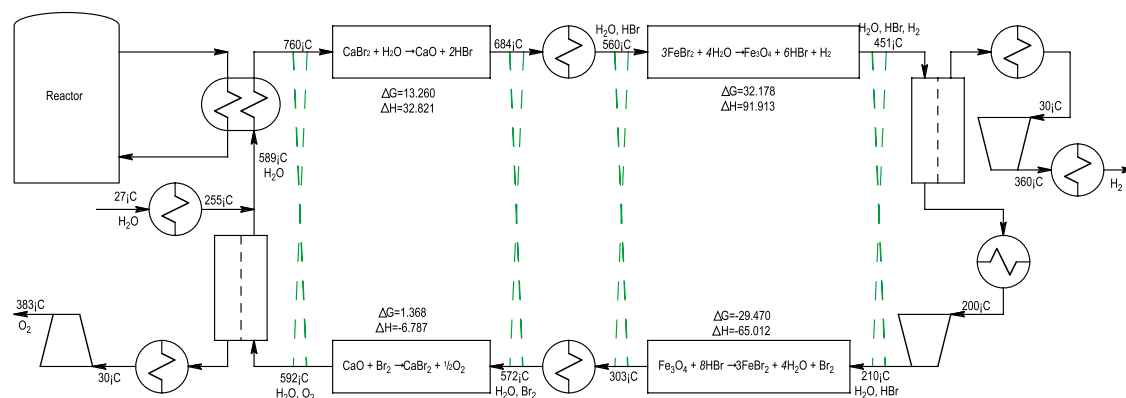


Fig. 2. Adiabatic UT-3 process flow diagram.

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 atm and the minimum steam pressure is 18.5 atm. 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 atm 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 backside 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% to 40%, depending upon the efficiency of the membrane separation processes. Higher overall efficiencies, 45% to 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.

2.6.2. 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 6. Attempts to use distillation were futile as sulfuric acid and hydrogen iodide react according to the reverse of reaction 6 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 3 shows a block flow diagram of the cycle based on this separation. Several investigators have studied the sulfur-iodine cycle 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.

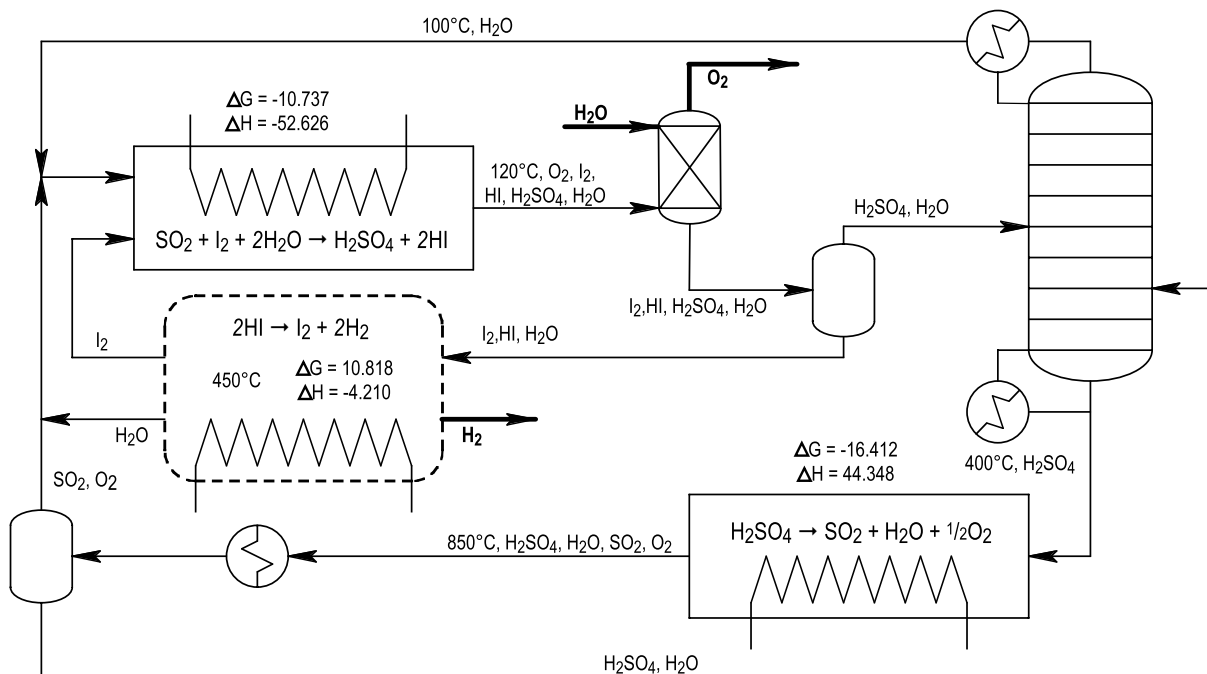


Fig. 3. Sulfur-iodine cycle process flow diagram.

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 7 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.

Subsequent to the cessation of development of the sulfur-iodine process in the U.S., 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 backup 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.

3. PLANS FOR PHASES 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 is shown in Table 5.

TABLE 5
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

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 optimize the process flowsheet to minimize 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.

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.

3.1. COLLABORATION WITH JAPAN

It would be advantageous, if some form of joint collaboration can be established with Japan. 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 our Japanese colleagues to perform the required nonsteady state analysis. After the work on the UT-3 process and the sulfur iodine process has been completed, we will have two processes from which to select a means of producing hydrogen using nuclear power.

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