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

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L. C. Brown, G. E. Besenbruch and K. R. Schultz
General Atomics
P.O. Box 85608
San Diego, CA 92186
lloyd.brown@gat.com

S. K. Showalter, A. C. Marshall and P. S. Pickard
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185

J. F. Funk
University of Kentucky
Lexington, KY 40506

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Abstract:

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 in a thermochemical water-splitting cycle.

We carried out a detailed literature search of all published thermochemical cycles, creating a searchable database with more than 100 cycles and 800 references. We developed screening criteria and did detailed evaluation to select two cycles that appear most promising, the Adiabatic UT-3 cycle and the Sulfur-Iodine cycle. We selected the Sulfur-Iodine cycle for further development.

We then conducted a broad-based assessment of the suitability of various nuclear reactor types to the production of hydrogen from water using the Sulfur-Iodine cycle. A basic requirement is the ability to deliver heat to the process interface heat exchanger at temperatures up to 900 °C. We developed a set of requirements and criteria, considering design, safety, operational, economic and development issues. We identified the gas-cooled reactor, the heavy liquid metal-cooled reactor and the molten salt-cooled reactor as suitable for coupling to the S-I cycle, selecting the helium gas-cooled reactor for our design.

In the third phase of this work, we are generating an integrated flowsheet describing a thermochemical hydrogen production plant powered by a high-temperature helium gas-cooled nuclear reactor. This will allow us to calculate the hydrogen production efficiency and capital cost and to estimate the cost of the hydrogen produced as a function of the nuclear plant cost.

1. Introduction

Combustion of fossil fuels provides 86% of the world's energy [1,2]. Drawbacks to fossil fuel utilization include limited supply, pollution, and carbon dioxide emissions, thought to be responsible for global warming [3,4]. Hydrogen is an environmentally attractive fuel that has the potential to displace fossil fuels, but contemporary hydrogen production is primarily based on fossil fuels. 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. The objective of this work is to find an economically attractive process for the production of hydrogen 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, could meet these goals.

This report describes work during the first phases 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 goal 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. In the second phase, all the basic reactor types were reviewed for suitability to provide the high temperature heat needed by the selected thermochemical water splitting cycle(s) for hydrogen production.

2. Thermochemical Water-splitting Process Selection

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.

$$H_2O \rightarrow H_2 + {}^1\!/_2O_2 \qquad \text{(2500°C min)} \tag{1}$$

At this temperature, only 10% of the water is decomposed. 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.

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

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \qquad \text{(120°C)} \tag{3}$$

$$2HI \rightarrow I_2 + H_2 \qquad \text{(450°C)} \tag{4}$$

$$H_2O \rightarrow H_2 + {}^1\!/_2O_2 \tag{1}$$

With a suitable catalyst, the high-temperature reaction (2) reaches 10% conversion at only 510°C, and 83% conversion at 850°C. Moreover, there is no need to perform a high temperature separation as the reaction ceases when the stream leaves the catalyst.

Energy, as heat, is input to a thermochemical cycle via one or more endothermic high-temperature chemical reactions. Heat is rejected via one or more exothermic low temperature reactions. Other thermally neutral chemical reaction may be required to complete the cycle so that all the reactants, other than water, are regenerated. In the S-I, cycle most of the input heat goes into the dissociation of sulfuric acid. Sulfuric acid and hydrogen iodide are formed in the endothermic reaction of H_2O, SO_2 and I_2, 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 is not sufficient for a cycle to be thermodynamically realizable. Each reaction must also have favorable ΔG (Gibbs free energy). A reaction is favorable if ΔG is negative, or at least not too positive. 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 possible to electrochemically force a non-spontaneous reaction; such a process is termed a hybrid thermochemical cycle. 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) $H_2O \rightarrow H_2 + {}^1/_2O_2$

2.1 Project databases

An important part of the preliminary screening effort dealt with organizing and presenting data in a easy to use form 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.

A second database was required to keep track of the thermochemical cycles. We had four 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 1 shows the organization of the database. A "cycle" represents a complete series of chemical reactions to produce water. "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. The database format makes it easy to search for commonality between various cycles (e.g. similar reactions, authors, compounds, etc.). The cycle database contains the details of the chemical reactions and process conditions, as well as the references to the cycles.

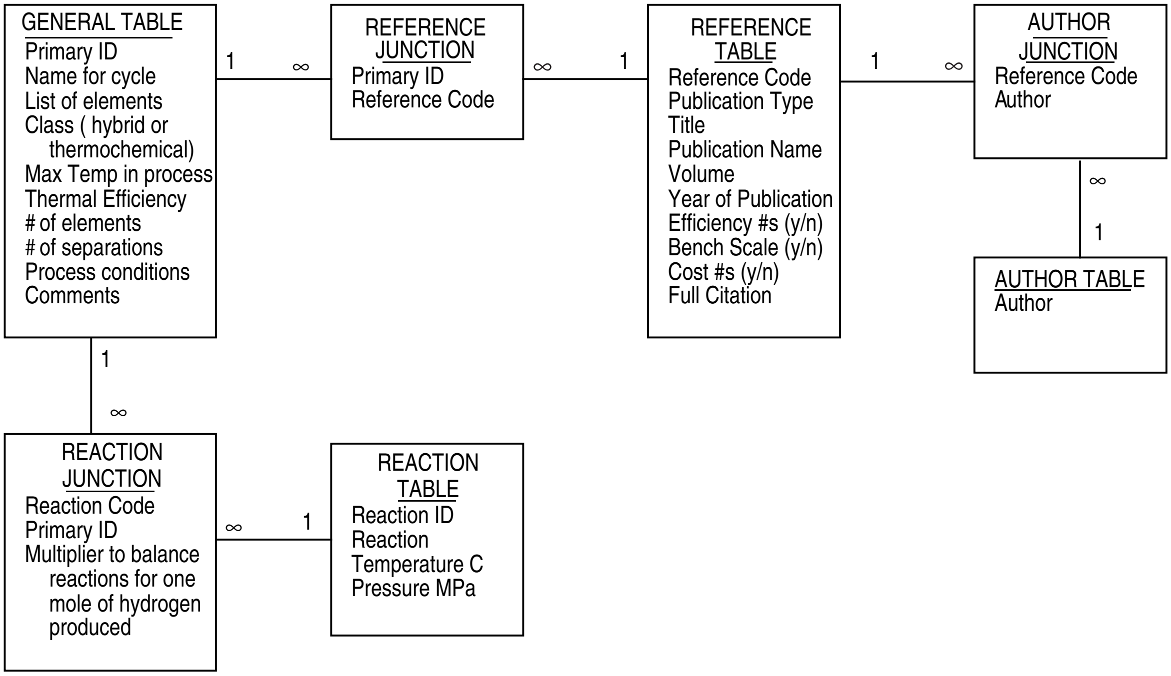

Figure 1. Database structural relationship.

Data were 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.
2. Next the authors are compared; if they are not represented they are added to the authors table.
3. Next the reference is added to the references table and assigned a unique reference ID.
4. The author junction table is then used to join the author ID with the reference ID.
5. The reference junction table is then used to join the reference ID to the general table entry.
6. Finally the reactions in the cycle are rearranged to fit our format, 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.
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.

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. Access to this database will be available via the Internet at the conclusion of this project.

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. Thermochemical generation of hydrogen is usually referred to 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. Moreover, some authors do not use the term water-splitting. It has proven to be most profitable to build up 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. 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 watersplitting or ((hydrogen or h2) 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 were for papers related to thermochemical water-splitting. The formal search 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.

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.
232	SCISEARCH	Science Citation Index Expanded
68	CEABA	Chemical Engineering And Biotechnology Abstracts
33	PROMT	Predicasts Overview of Markets and Technology
28	INSPHYS	INSPHYS is a supplementary file to the INSPEC database.

Interest in thermochemical watersplitting has varied greatly with time. Figure 2 indicates when the references in the database were published. The initial interest, in the early 1960's [8], was by the military, which was interested in the use of a portable nuclear reactor to provide logistical support. Interest boomed in the 1970's 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.

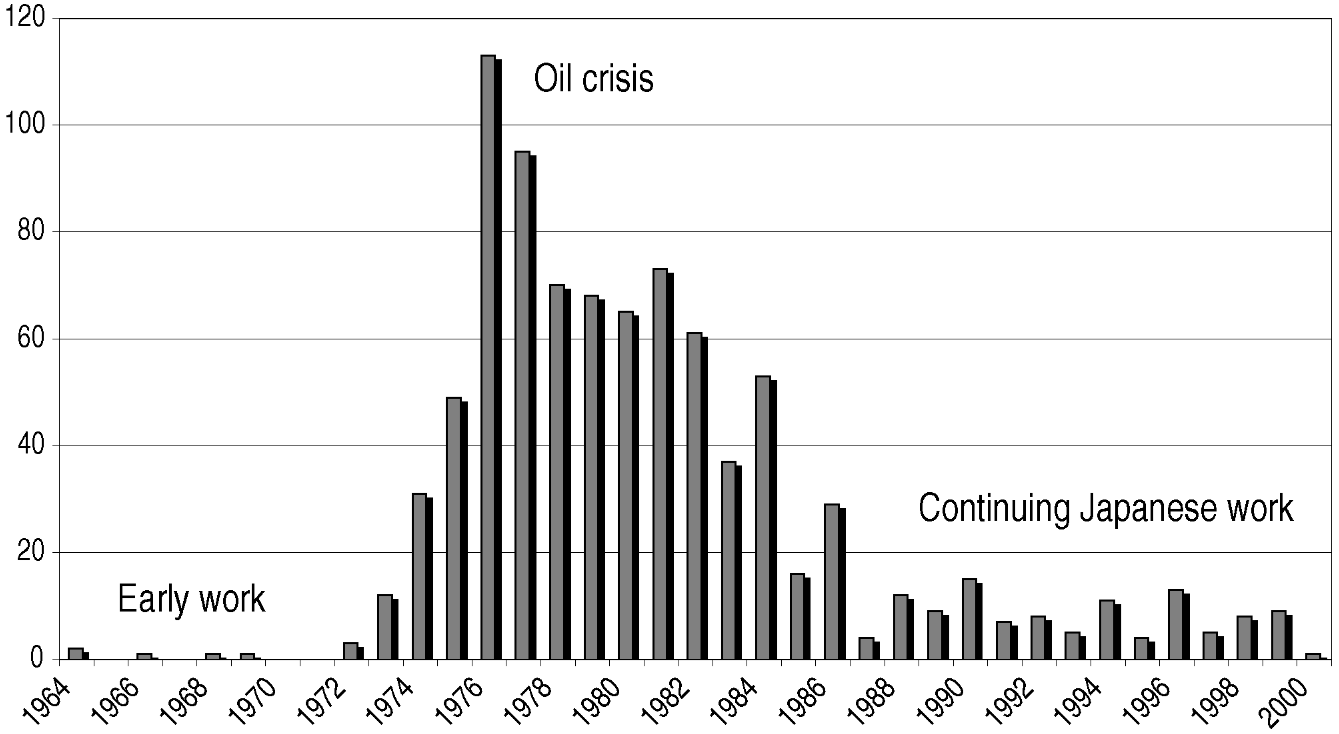

Figure 2. Publications by year of issue.

2.3 Preliminary screening criteria

The literature search turned up a large number of cycles (115), far too many to analyze in depth. It was necessary to establish meaningful and quantifiable screening criteria and to establish metrics by which each proposed cycle could be evaluated. The criteria ultimately agreed upon are given in Table 2. The translation of each metric to a score is given in Table 3. Equal weighting was given to each criterion in calculating the final score.

One of the originally proposed criteria was left out because a simple metric could not be devised. 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 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 metric 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

Table 2. Rational for development of first round screening criteria.

Desirable Characteristic	Rational	Metric
1 Higher ranked cycles will have a minimum number of chemical reaction 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 steps 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 in 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 costs on hydrogen production efficiency and cost must be considered.	Score is based on 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 been the subject of many papers from many authors and institutions.	Higher thermal efficiency can not 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 is 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 3. 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 soilds 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	<300°C or >1300°C	300°-350°C or 1250°-1300°C	350°-400°C or 1200°-1250°C	400°-450°C or 1150°-1200°C	450°-500°C or 1100°-1150°C	500°-550°C or 1050°-1100°C	550°-600°C or 1000°-1050°C	600°-650°C or 950°-1000°C	650°-700°C or 900°-950°C	700°-750°C or 850°-900°C	750°-850°C
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 flowsheet		Detailed cost calculations based on detailed flowsheets available from one or more independent sources		

† Interpolate scores between defined scale points

operation. In this case, we considered there to be just one reaction, for the purpose of calculating thescore. 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, we considered there to be one reaction, independent of the way the cycle was described in the literature.

<u>Metric 2 – Number of chemical separation steps.</u> The number of separations for a cycle was determined from the number of separations required for each chemical reaction which is assumed to yield a mixture of its reactants and products. After phase separation, there is one less separation than there are components, if the components must be separated before the next reaction. As an example, consider 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) $Fe3O4(s) + 8HBr(g) \rightarrow Br2(g) + 3FeBr2(s) + 4H2O(g)$ (210°C)

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 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. 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.

<u>Metric 3 – Number of elements.</u> Every element found in any reaction of the cycle was listed and counted. Oxygen and hydrogen were ignored. Catalysts were also ignored.

<u>Metric 4 – Elemental abundance.</u> Elements were ordered by their atomic abundance in the earth's crust or atmosphere and separated into groups differing by roughly an order of magnitude in abundance. The score was based on the least abundant element.

<u>Metric 5 – Corrosive chemicals.</u> 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 stationary 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.

Metric 7 – Maximum cycle temperature. 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 ΔG for a non-electrolytic reaction. 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 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.

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. 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 1,600°C. 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 4, along with their scores. One literature reference is included for each cycle. Details for these cycles are given in Table 5.

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 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].

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 6, 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. 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.

The nuclear reactor to be used has not been defined except to the point that it will be a high temperature reactor. The chemical process will likely 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 3 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 of the coolant or the process as a function of the amount of heat transferred. The coolant and process are in countercurrent flow heat exchange.

Table 4. Short list of cycles and their scores

Cycle#	Name	Class	Max Temp	Elements	#Elems	#Seps	#Rxns	1 Rxns	2 Seps	3 Elems	4 Abund	5 Corr	6 Solids	7 Temp	8 Pubs	9 Tests	10 Data	Total
1.	Westinghouse	H	850	S	1	2	2	10	8	10	9	5	10	9	10	6	8	85
2.	Ispra Mark 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	T	750	Br,Ca,Fe	3	3	4	6	7	8	7	5	6	10	10	10	10	79
4.	GA Sulfur-Iodine	T	800	I,S	2	3	3	9	7	9	4	5	10	10	10	6	8	78
5.	Julich Center EOS	T	800	Fe,S	2	3	3	9	7	9	9	9	6	10	3	3	3	68
6.	Tokyo Inst. Tech. Ferrite	T	1000	Fe,Mn,Na	3	2	2	10	8	8	8	10	10	6	2	2	0	64
7.	Hallett Air Products 1965	H	800	Cl	1	3	2	10	7	10	10	5	10	10	0	0	0	62
8.	Gaz de France	T	825	K	1	3	3	9	7	10	9	5	6	10	2	2	2	62
9.	Nickel Ferrite	T	1000	Fe,Ni,Mn	3	0	2	10	10	8	7	10	6	6	0	3	0	60
10.	Aachen Univ Julich 1972	T	800	Cr,Cl	2	3	3	9	7	9	7	5	6	10	2	2	2	59
11.	Ispra Mark 1C	T	900	Br,Ca,Cu	3	4	4	6	6	8	7	5	10	8	2	3	3	58
12.	LASL-U	T	700	C,U	2	3	3	9	7	9	4	10	6	9	1	3	0	58
13.	Ispra Mark 8	T	900	Cl,Mn	2	3	3	9	7	9	8	5	3	8	3	2	3	57
14.	Ispra Mark 6	T	800	Cl,Cr,Fe	3	4	4	6	6	8	7	5	6	10	2	3	3	56
15.	Ispra Mark 4	T	800	Cl,Fe	2	4	4	6	6	9	10	5	0	10	3	3	3	55
16.	Ispra Mark 3	T	800	Cl,V	2	3	3	9	7	9	7	5	0	10	2	3	3	55
17.	Ispra Mark 2 (1972)	T	800	C,Na,Mn	3	3	3	9	7	8	8	5	0	10	2	3	3	55
18.	CO/Mn3O4	T	977	C,Mn	2	3	3	9	7	9	8	9	6	7	0	0	0	55
19.	Ispra Mark 7B	T	1000	Cl,Fe	2	5	5	3	5	9	10	5	10	6	0	3	3	54
20.	Vanadium Chloride	T	700	Cl,V	3	5	4	6	5	8	7	5	6	9	3	2	2	53
21.	Ispra Mark 7A	T	1000	Cl,Fe	2	5	5	3	5	9	10	5	6	6	3	3	3	53
22.	GA Cycle 23	T	850	S	2	4	5	3	6	9	9	5	10	9	0	0	0	51
23.	US-Chlorine	T	993	Cl,Cu	2	3	3	9	7	9	7	6	5	7	0	0	0	50
24.	Ispra Mark 9	T	450	Cl,Fe	2	8	3	9	2	9	10	5	3	4	2	3	3	50
25.	Ispra Mark 6C	T	800	Cl,Cr,Cu,Fe	4	5	5	3	5	6	7	5	6	10	2	3	3	50

Table 5. 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

Table 5 (Continued). Reaction Details For Cycles

Cycle	Name	T/E*	T °C	Reaction	F†
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	$H_2S \rightarrow S + H_2(g)$	1
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	$4MnO2(s) \rightarrow 2Mn_2O_3(s) + O_2(g)$	$^1/_2$
		T	800	$Mn_2O_3 + 4NaOH \rightarrow 2Na_2O.MnO_2 + H_2(g) + H_2O$	1
18	Ispra CO/Mn3O4 [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.

†: Multiplier for one mole of H_2O decomposed

Table 6. 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

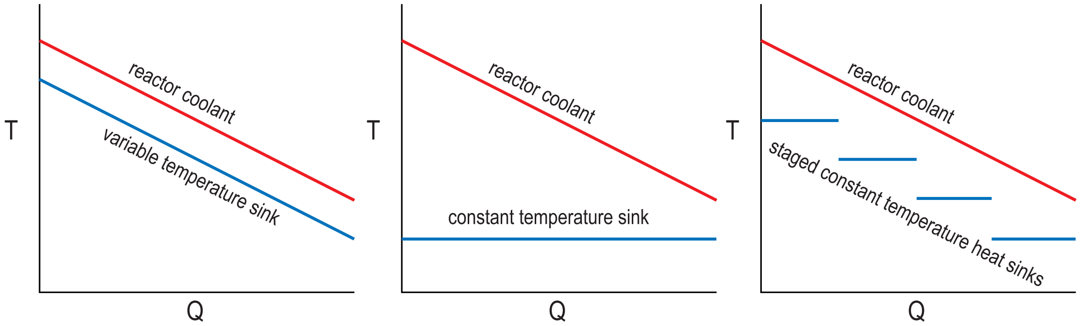

Figure 3. Matching of thermochemical cycle to reactor

The first process is well matched as the temperature-enthalpy curves of the process and coolant are parallel. Since the coolant enthalpy is in the form of sensible heat, its T–H 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 equilibrium over the temperature range but as heat is input, the concentration of reactants decreases and products increases. This is the type of T-H curve expected from homogeneous chemical reactions and from 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 chemical reactions that occur at different temperatures, or to perform 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. However, efficient electrochemical processes require thin membranes between the anode and cathode. This limits efficient electrochemical processes to small electrode areas. Commercial electrochemical processes certainly exist, but they are not energy efficient in large sizes.

2.7 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 1970’s and essentially all work has been performed in Japan. Work has continued to this date with the latest publication last year. 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 is shown in Figure 4. The four chemical reactions take place in four adiabatic fixed 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 into the gas stream which traverses through the four chemical reactors, three process heat exchangers, two membrane separators and the recycle compressor before the gases are recycled to the reactor heat exchanger. 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 passes through the unreacted solid and exits. After some time, perhaps an hour, the flow paths are switched and the chemical reactors switch functions. The reaction front reverses direction and travels back toward the end that had previously been the entrance.

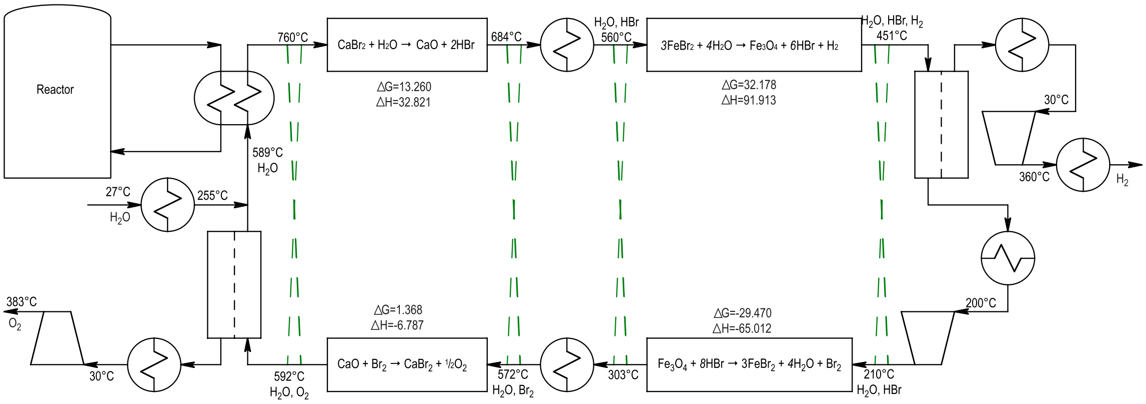

Figure 4. Adiabatic UT-3 Process Flow Diagram

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 steam flow provides the additional function of sweeping the products away from the reaction front and thus shifting the reaction equilibrium towards completion, 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%. 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 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. The solids must be chemically available to gas phase reactions yet physically stable while undergoing repeated cycling between the oxide and bromide forms. Membranes must be developed that are suitable for large scale use. There is limited potential for future process improvements as the adiabatic implementation is already quite simple. There is little room for efficiency improvement as the process already operates at the maximum $CaBr_2$ operating temperature

<u>Sulfur-Iodine Cycle.</u> The Sulfur-Iodine cycle was developed at General Atomics and first described in the mid 1970's. It was rejected by early workers due to difficulties

encountered separating the hydrogen iodide and sulfuric acid produced in reaction 3. The key to successful implementation of the cycle was using an excess of molten iodine to give a two-phase solution, a light phase containing sulfuric acid and a heavy phase containing hydrogen iodide and iodine. Figure 5 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.

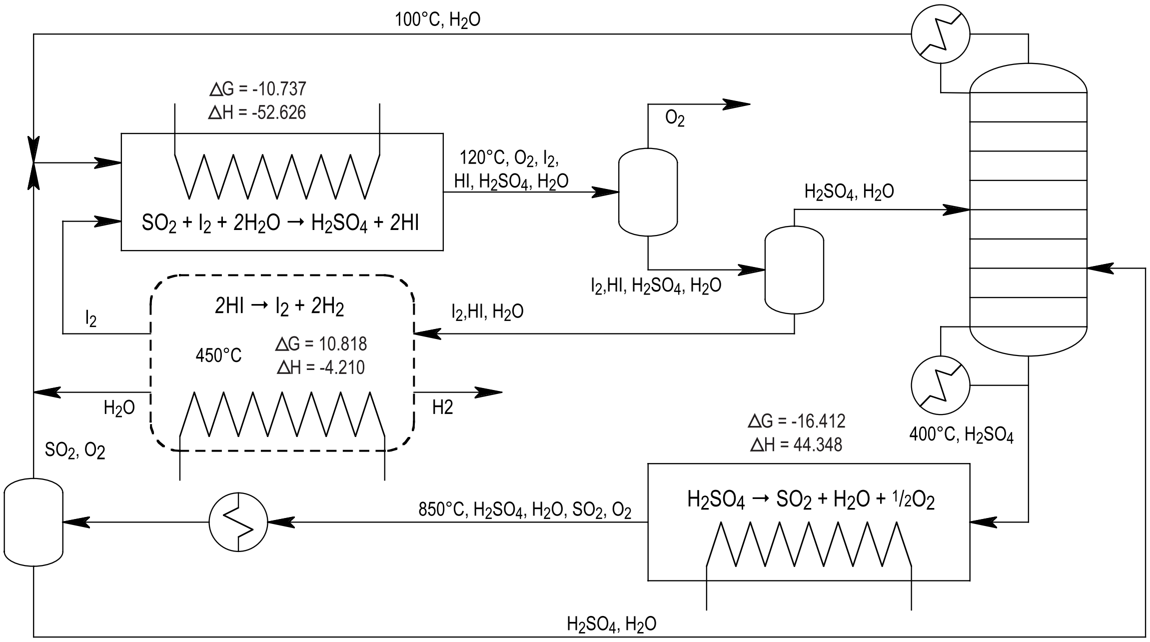

Figure 5. Sulfur-Iodine Cycle Process Flow Diagram

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 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 solely 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.

Researchers at the University of Aachen demonstrated experimentally, that the hydrogen iodide need not be separated from iodine before the decomposition step. 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. The Japanese consider the Sulfur-Iodine cycle to be a back-up for the UT-3 cycle which is the main focus of their investigations. Effort on UT-3 on our part would contribute relatively little to this activity. For these reasons, we have selected the Sulfur-Iodine cycle for our project. In the next phases of this study 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.

3. Selection of Nuclear Heat Source

Several types of nuclear reactors are capable of producing heat in the temperature range of interest. We analyzed the characteristics of the various types of reactors as heat sources for a sulfur-iodine cycle. Ideally, the recommended reactor technology would require minimal technology development to meet the high temperature requirement. Furthermore, the reactor system should not present any significant design, safety, operational, or economic issues.

At present, the plan is to use an intermediate helium loop between the reactor coolant loop and the hydrogen production system. This assures that any leakage from the reactor coolant loop will not contaminate the hydrogen production system or expose plant personnel to radiation from the primary loop coolant. It also assures that the corrosive process chemicals cannot enter the core of the nuclear reactor. Thus, the heat exchanger interface, sets the boundary conditions for selection of the reactor system. The principal requirement is the temperature requirement for the sulfur-iodine cycle, which must account for the temperature drop between the core outlet and the point of application in the hydrogen production system. We assumed a required temperature of 900 °C.

The reactor coolant becomes a primary consideration for determining which concepts are most appropriate. Furthermore, the basic reactor types are generally classified by the coolant type. Given these considerations, reactor categories can be delineated by nine basic coolant types identified in Table 7. The reactor/coolant types include pressurized water-cooled reactors, boiling water-cooled reactors, alkali liquid metal-cooled reactors, heavy liquid metal-cooled reactors, gas-cooled reactors, organic-cooled reactors, molten salt-cooled reactors, liquid-core reactors, and gas-core reactors. Four assessment stages were used in this study:

> **Stage 1:** The level of development of the basic reactor types was reviewed. Speculative concepts with extreme developmental requirements could be eliminated at this stage.

Table 7. Reactor Types Considered in the Assessment

1. Pressurized Water Reactors [21]
    - Pressurized Water Reactors (light and heavy water) [22]
    - Supercritical Pressurized Water Reactors [23]
2. Boiling Water Reactors [21]
    - Boiling Water Reactors (light and heavy water) [21]
    - Boiling Water Reactors with Superheat [24, 25]
3. Organic-Cooled Reactors [24, 25]
    - Diphenyl
    - Other organic coolants
4. Alkali Liquid Metal-Cooled reactors [21, 26]
    - Lithium-cooled
    - Other (Na, K, NaK)
5. Heavy Liquid Metal-Cooled Reactors [25, 27, 28]
    - Lead-bismuth
    - Other (Pb, Bi, Sn, Hg)
6. Gas-Cooled Reactors [24, 25, 29]
    - Noble gasses (He, Ar)
    - Other gasses (CO_2, H_2, N_2 , Air, Ar, Steam)
7. Molten Salt-Cooled Reactors [21,22,25]
    - $2LiF\text{-}BeF_2$
    - Other salts
8. Liquid-Core Reactors [24, 25, 30]
    - Molten Salt-Core
    - Liquid Metal-Core
    - Aqueous-Core
9. Gas-Core Reactors [31]
    - UF_6
    - Other gas/fuel (UF_4, U-plasma)

Stage 2: Coolant properties were examined to identify merits, issues, and limitations. Fundamental limitations of coolant choices could result in the elimination. A baseline coolant option was selected for each reactor type; e.g., Li was selected from Na, Li, NaK, and K for alkali metal-cooled reactors.

Stage 3: The reactor types were subjectively assessed based on the five requirements and five important criteria given in Table 8. A subjective grade is given for each reactor type (A through F) for each assessment criterion.

Stage 4: For the final stage, developmental requirements are reviewed for the top three of the remaining candidates. Based on this analysis a baseline concept was recommended as a heat source for the sulfur-iodine cycle.

Table 8

(a) Basic Requirements
1. Chemical compatibility • Compatibility of coolant with primary loop materials and fuel.
2. Coolant Stability • Molecular stability of coolant at operating temperatures in a radiation environment.
3. Pressure requirements • Pressure limitations for primary loop.
4. Nuclear requirements • Unacceptable parasitic neutron capture by coolant, high neutron activation, fission product effects, gas buildup, etc.
5. Feasibility • Basic feasibility, general development requirements, and development risk.
(b) Important Criteria
1. Safety 2. Operational Issues 3. Capital Costs 4. Intermediate Loop Compatibility 5. Other merits and Issues

3.1 Status and Characteristics of Reactor Types

Before embarking on a study of a specific reactor concept for hydrogen production, we did an assessment of all possible reactor candidates. We explored a broad range of reactor concepts and options, from the highly conventional to the highly speculative. The principal reactor categories include pressurized water-cooled reactors, boiling water-cooled reactors, alkali liquid metal-cooled reactors, heavy liquid metal-cooled reactors, gas-cooled reactors, organic-cooled reactors, molten salt-cooled reactors, liquid-core reactors, and gas-core reactors. Gas-core reactors were considered too speculative to be seriously considered for hydrogen production.

Reactor coolants and heat transport fluids should have low melting points, good heat transport properties, and low potential for chemical attack on vessels and piping. Reasonable operating pressures and compositional stability at operating temperature are also important characteristics. Other desirable properties include low toxicity and low fire and explosion hazard. Reactor coolants must also possess desirable nuclear properties, such as radiation stability and low neutron activation. For thermal reactors, low parasitic capture cross sections are required. If the coolant is to serve as a moderator, low atomic number constituents are desirable. Property values and characteristics for potential reactor coolants are presented in Table 9. Pressurized water and boiling water reactors could not reasonably expect to achieve the temperatures needed for the S-I cycle. Organic coolants were similarly found to be not well-suited. For the alkali metal-cooled reactors, lithium was selected as the preferred coolant due to its low vapor pressure at high temperature. For the heavy metal-cooled reactors, the PbBi eutectic was selected due to its lower melting point and lower radiotoxicity than Pb or Bi alone. For the gas-cooled reactors, helium was selected as preferred due to its chemical inertness at high temperature

Table 9 (a). Reactor Coolant Basic Properties

Coolant	**Molecular Weight**	**Density* (g/cc)**	**σ_{th} parasitic (b)**	**Neutron activation**	**Radiolytic Decomposition**	**Hazards**		
						Toxic	**Fire**	**Explosion**
Water								
H_2O	18	1	0.66	Some	Some	No	No	No
D_2O	20	1.1	0.001					
Organic								
Diphenyl	154	0.86	0.33	low	Yes	No	No	No
Alkali Metal								
Li	7	0.53	71	High	Stable	Yes	Yes	Yes
Na	23	0.82	0.525					
NaK	-	0.74	~0.5					
K	39	0.70	2.07					
Heavy Metal								
Sn	118	6.5	0.625	High	Stable	No	N0	No
Hg	200	13.6	380			High		
Pb	207	11.4	0.17			Yes		
Bi	209	9.75	0.034			No		
PbBi	-	~10	~0.1			Yes		
Gases								
H_2	2	0.00009	0.332	Low	Stable	No	High	High
He	4	0.00018	0.007	No	Stable	No	No	No
N_2	14	0.0013	1.88	No	Stable			
Ar	40	0.0018	0.66	Yes	Stable			
CO_2	44	0.0015	0.0038	Some				
Air	-	0.0013	~1.3	Yes				
Steam	18	0.00056	0.66	Some	Some			
Molten Salt								
$2LiF\text{-}BeF_2$	-	~2	-	Yes	Stable	Yes	No	No
Liquid Core								
Aqueous	-	~1	-	Fission products Very high	Some	Yes	No	No
Liquid Metal	-	~10	-		Stable	Yes	Yes	Yes
Molten Salt	-	~2.5	-		Stable	Yes	No	No

* @ ambient temperature

Table 9 (b). Reactor Coolant Thermal and Chemical Properties

Coolant	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure (MPa)*	Heat transport properties	Thermal stability Limit (K)	Chemical attack @ 900 °C
Water						
H_2O	0	100	13.7	Very good	Stable	Yes
D_2O	0	101	13.7		Stable	
Organic						
Diphenyl	69	255	0.2	Good	750	Yes
Alkali Metal						
Li	181	1331	10^{-10}	Excellent	Stable	Yes (Nb alloys may be suitable)
Na	98	881	5×10^{-6}			
NaK	-11	784	$\sim 10^{-4}$			
K	64	761	10^{-4}			
Heavy Metal						
Sn	232	2270	$<10^{-14}$	Excellent	Stable	Some (Coolant additives may be suitable)
Hg	-38.5	358	0.07			
Pb	327	1740	10^{-13}			
Bi	271	1570	10^{-11}			
PbBi	125	1670	10^{-11}			
Gas						
H_2	-	-	-	Poor	Stable	Yes
He	-	-	-		Stable	No
N_2	-	-	-		Stable	Yes
Ar	-	-	-		Stable	No
CO_2	-	-	-		< 850	Yes
Air	-	-	-		< 850	Yes
Steam	0	100	-		-	High
Molten Salt						
$2LiF\text{-}BeF_2$	457	1397	$< 10^{-9}$	Excellent	Stable	Yes
Liquid Core						
Aqueous	-	-	~10	Excellent	Some fuel precipitation	Yes
Liquid metal	~300	~1500	Low		Some fuel precipitation	Yes
Molten Salt	497		$< 10^{-9}$		Stable?	Yes

* @ saturation, 600 K

Using the requirements and criteria presented in Table 8, a subjective grade was assessed for each of the remaining candidate reactor options. A brief discussion of the assessment basis is presented here, and a summary of the assessment grades for each requirement and criteria is provided in Table 10. For each consideration, reactor concepts were graded using the following rating scheme:

Grading basis for requirements	**Grading basis for criteria**
A: -Projected or demonstrated feasible	**A**: - Ideal
B: - Promising, but development needed	**B**: - Good, not optimum
C: - Possible, but significant development needed	**C**: - Issues or poorly suited, but possible
F: - Not feasible (eliminate from consideration)	**F**: - Unacceptable (eliminate from consideration)

Table 10. Assessment of Reactor Concepts for Sulfur-Iodine Thermochemical Cycle

Coolant	Gas	Salt	Heavy metal	Alkali metal	Molten core	PWR	BWR	Organic	Gas core
1. Materials compatibility	A	B	B	C	B	-	F	-	-
2.Coolant stability	A	A	A	A	B	-	-	F	-
3. Operating Pressure	A	A	A	A	A	F	-	-	-
4.Nuclear issues	A	A	A	B	B	-	-	-	-
5. Feasibility-development	A	B	B	C	C	-	-	-	F
1. Safety	B	B	B	**B^-**	B	-	-	-	-
2. Operations	A	B	B	B	C	-	-	-	
3. Capital costs	**B^-**	B	B	C	C				
4. Intermediate loop compatibility	A	B	B	B	B	-	-	-	-
5. Other merits and issues	B	B	B	B	B	-	-	-	-
Unweighted Mean Score (A=4.0)	3.67	3.30	3.33	2.87	2.80	N/A	N/A	N/A	N/A

From the preceding analysis, the gas-cooled reactors (GCR), molten salt-cooled reactors (MSCR), and heavy metal-cooled reactors (HMR) appear to be the most promising. An estimate of the relative development cost of the three concepts is instructive. For the purpose of selecting a baseline concept, a simple method for comparing development was used. The expected development cost trends for MSCR and HMR systems were compared relative to GCR development costs. The following simple indictors were used:

0	Approximately the same development cost as for gas-cooled reactors
-1,-2	Lower development cost than for gas-cooled reactors
+1,+2	Higher development cost than for gas-cooled reactors

The following development activities were identified:

1. Materials development
2. Fuel development
3. Component development
4. System design
5. Fabrication facility development

In order to allow for uncertainty in the assessment, maximum and minimum development cost trends were assessed relative to GCR maximum and minimum development costs. The results of this assessment are presented in Table 11.

<u>Materials Development</u>. Materials development refers to coolant compatibility issues. Gas-cooled reactors have demonstrated acceptable materials compatibility for more than a decade of operation (AVR) in the required temperature regime. Molten salt and heavy metal coolant compatibility looks promising. On the other hand, demonstrated molten salt compatibility close to the desired temperature range was limited to about two years. Given this lack of long term operational experience, additional development may be required for the MSCR (+1). Russia has many years of operational experience with heavy metal coolants, but operating temperatures were much lower than 900°C. Additional development work may be needed to achieve 900°C for the HMR (+1).

<u>Fuel Development</u>. The required coolant temperature is somewhat higher than for U.S. HTGR experience and could result in higher fuel temperatures than demonstrated for HTGR designs. Internationally, the AVR has demonstrated excellent fuel performance in the required temperature regime, and the HTTR is currently ramping temperature performance up to the expected operating temperature of 950°C. A significant effort in developing zirconium carbide coated fuel particles is underway in Japan.

The excellent heat transfer characteristics of molten salt coolants may result in less demanding requirements on the fuel. Optimistically, the fuel already developed for gas-cooled reactors may be used for the MSCR, but the MSCR is a new and undeveloped concept and additional development work cannot be ruled out (0). Fuel performance data for HMRs is totally lacking in the required temperature range, and appreciable development work is projected for HMRs (+2).

Component Development. Some component development is required for all three concepts, but no significant component development issues, relative to GCRs, are identified for the MSCR or the HMR. The lack of experience with these systems, in the required temperature range, implies the possibility of long term unexpected component development costs (+1).

System Design Development. Full system designs for high temperature GCRs have been developed, whereas the MSCR is an entirely new concept; significant MSCR system design development is anticipated (+2). The Russians have carried out appreciable design development work for a commercial HMR. If the higher temperature capability required for the sulfur-iodine cycle does not alter the design significantly, it is possible that additional system design work will be minimal. Nonetheless, a more detailed examination of the system requirements for a high temperature HMR may lead to significant system design development (+1).

Fabrication Facility Development. Fuel fabrication facilities for production of coated fuel particles that can be used in GCRs exist in the U.S. at B&W and NSF. They have been in operation, producing fuel for the Navy, for more than twenty years. A complete fuel fabrication facility for the HTGR existed at General Atomics, but has been dismantled. Internationally, fuel fabrication facilities existed in Germany for the Pebble Bed Reactor fuel and the technology is being transferred to South Africa. Developmental fuel fabrication facilities exist in Japan and fuel fabrication facilities are being developed in Russia. The GCR, having been operated commercially, requires no fuel fabrication development effort. Although a commercial fuel fabrication facility must be constructed, the fuel fabrication technology is fully documented.

If, indeed, MSCRs use the same fuel as GCRs, no fabrication development will be necessary. The assumption that MSCRs can use GCR fuel is based on the documented resistance of graphite to $2LiF-BF_2$. Although the fuel elements and coated particles are fully graphitized, the fuel compacts are not. Optimistically no fuel fabrication technology need be developed (0).

Fuel fabrication facilities will need to be developed for the HMR. Some facilities capable of producing HMR fuel probably exist in Russia, but this fuel never operated at the required temperatures. Some fuel fabrication technology will probably need to be developed (+1).

From Table 11 we observe that the GCR appears to result in the lowest development cost and risk.

Table 11. Development Cost Trends Relative to GCRs

	Materials	**Fuel**	**Component**	**System**	**Fab.-facility**	**Total**
Molten salt	**+1**	**+1**	**+1**	**+2**	**0**	**+6**
Heavy metal	**+2**	**+2**	**+1**	**+1**	**+1**	**+7**

3.2 Conclusions and reactor selection

Based on the forgoing discussion, the following conclusions and recommendations are made:

PWR, BWR, Organic-Cooled, and Gas-Core Reactors – Not Recommended

- From the preceding analysis we conclude that all PWR approaches are impractical in that enormous system pressures are required to obtain 900°C coolant temperatures.
- The highly corrosive nature of 900°C steam eliminates BWRs from consideration.
- Organic-cooled reactors are not recommended as a heat source for the sulfur-iodine thermochemical cycle because organic coolants dissociate at temperatures well below the required cycle temperature.
- Gas core reactors were not considered because the approach requires unproven technology at a fundamental level and the development risk is too great for the goals of this program.

Liquid-Core and Alkali Metal-Cooled Reactors – Significant development risk

- Although the liquid-core reactor technology is promising for operation at the required temperatures, the circulation of radiologically hot fuel/coolant presents many operational and developmental issues. At this stage the molten core is judged to be a possible approach, but it is not retained as a strong alternative.
- Alkali metal-cooled reactors are also possible candidates, but the general corrosiveness of alkali metals at very high temperatures is an important issue. At this stage, the technology risk and development cost are judged to be significant. Furthermore, if special alloys and complex fuel elements are required, the capital cost required to produce a system capable of meeting performance requirements may be significant. Positive void coefficients, fire and explosion hazards, coolant activation, and thaw requirements are additional undesirable features of alkali metal coolants. For these reasons, alkali metal-cooled reactors are considered as possibilities, but not a strong alternative.

Heavy Metal and Molten Salt-Cooled Reactors – Promising

- Both HMRs and MSCRs appear to be promising candidates, but much uncertainty in their development requirements places these approaches in the promising alternative category.

Gas Cooled Reactors – Baseline choice

- Based on Tables 10 and 11, helium gas cooled reactors appear to require the least development work and present the lowest development risk. The underlying reasons for their suitability for the high temperature sulfur-iodine cycle are: (1) helium is chemically inert, and (2) gas-cooled reactors have been successfully operated for a number of years in the required temperature range. Helium gas-cooled reactors are recommended as the baseline choice for a reactor heat source for a sulfur-iodine thermochemical cycle for hydrogen production.

4. Conclusions and Plans for Project Completion

We carried out a detailed literature search of all published thermochemical cycles, creating a searchable database with 115 cycles and 800 references. We developed screening criteria and did detailed evaluation to select two cycles that appear most promising, the Adiabatic UT-3 cycle and the Sulfur-Iodine cycle. The UT-3 process has predicted efficiency of 35% to 40%. The Sulfur-Iodine cycle remains the cycle with the highest reported efficiency, 52%, with process improvements suggested that could increase the efficiency and lower the capital cost. We have selected the Sulfur-Iodine cycle thermochemical water-splitting process as the cycle best suited for matching to an advanced high temperature nuclear reactor heat source.

We then conducted a broad-based assessment of the suitability of various nuclear reactor types to the production of hydrogen from water using the Sulfur-Iodine cycle. A basic requirement is the ability to deliver heat to the process interface heat exchanger at temperatures up to 900 °C. We developed a set of five requirements and five criteria to carry out the assessment, considering design, safety, operational, economic and development issues in our evaluation. The Helium Gas-cooled Reactor, the Heavy Metal-cooled Reactor and the Molten Salt-cooled Reactor emerged as being well-suited for coupling to the Sulfur-Iodine cycle. The Helium Gas-cooled Reactor is much further developed than the other two candidates and two versions (the Modular Helium Reactor and the Pebble Bed Modular Reactor) are being developed for electricity production. They could be used for thermochemical production of hydrogen with no major additional development needed. We selected the helium gas-cooled reactor for coupling to the sulfur-iodine cycle.

To complete this project we must now carry out a preliminary engineering design of the S-I chemical process and use that design to estimate the cost and efficiency of the resulting water-splitting cycle. The preliminary engineering design of the process defines the connectivity of the chemical flowsheet. Each piece of process equipment is indicated and each flow stream 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 to be done is developing the material and energy balances for the process. A chemical process simulator (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. A key to minimizing the hydrogen cost is to maximize the efficiency of energy utilization, while minimizing the cost of the plant equipment.

As portions of the process design mature, we will define equipment specifications for the chemical process equipment. These specifications will form the basis for the cost estimates. The capital equipment costs will be estimated using standard chemical engineering techniques based on process equipment sizes and materials. All the information necessary to specify the process equipment, to this level of detail, will be available from the optimized mass and energy balance.

The key components in estimating the hydrogen production costs are the capital costs of the chemical plant and the nuclear power costs. 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. The result of this work will be an evaluation of the process efficiency and an estimate of the cost of hydrogen.

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

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** (1966) 336-342.

[9] Yalcin, S., “A review of nuclear hydrogen production,” Int. J. Hydrogen Energy, **14**(8) (1989) 551-561.

[10] Yoshida, K., H. Kameyama, et al., “A simulation study of the UT-3 thermochemical hydrogen production process,” Int. J. Hydrogen Energy **15** (1990) 171–178.

[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** (1977) 7–15

[13] Beghi, G.E., “A decade of research on thermochemical hydrogen at the joint research center, Ispra,” Int. J. Hydrogen Energy **11** (1986) 761–771.

[14] Besenbruch, G.E., “General Atomic sulfur-iodine thermochemical water-splitting process,” Am. Chem. Soc., Div. Pet. Chem., Prepr. 271 (1982) 48–53.

[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 (1995) 325–330.

[18] Bamberger, C.E., “Hydrogen production from water by thermochemical cycles; a 1977 update,” Cryogenics **18** (1978) 170–183.

[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** (1984) 457–472.

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

[21] V. Nero, Jr., *A Guidebook to Nuclear Reactors*, U. of Cal. Press, Berkeley, 1979.

[22] W. Forsberg and A. M. Weinberg, “Advanced Reactors, Passive Safety, and Acceptance of Nuclear Safety,” Annu. Rev. Energy **15**, pp. 133-152

[23] M. Simnad, *Fuel Element Experience in Nuclear Power Reactors*, Gordon and Breach Science Publ., NY, 1971.

[24] S. Glasstone and A. Sesonske, *Nuclear Reactor Engineering*, Van Nostrand Reinhold Co., NY, 1967.

[25] Bleuel, J. Scott, and L. Sevingy, *Introduction to the ALMR/PRISM,* http://www.nuc.berkeley.edu/~gav/almr/01.intro.html. November 2000.

[26] M. S. El-Genk, *A Critical Review of Space Nuclear Power and Propulsion 1984-1993*, American Institute of Physics, NY, 1994.

[27] M. I. Bugreev, et. Al., *Analysis of Risks Associated with Nuclear Submarine Decommissioning, Dismantling, and Disposals*, pp. 261-264, A. A. Sarkisov and A. Tournyol du (eds.), Kluver Academic Publishers, Netherlands, 1999.

[27] K. Kemm, *Development of the South Africa Pebble Bed Modular Reactor System*, http:www.uilondon.org/sym/1999kemm.htm, November, 2000.

[29] M. M. El-Wakil, *Nuclear Power Engineering,* McGraw-Hill Book Co., NY, 1962.

[30] J. A. Angelo and D. Buden, *Space Nuclear Power*, Orbit Book Co., Malabar, FL, 1985.

[31] S. Koshizuka and Y. Oka, “Supercritical-Pressure, Light-Water-Cooled Reactors for Economical Nuclear Power Plants,” Prog. Nucl Ener. **32**, pp. 547-554, 1998.

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