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Nuclear Production of Hydrogen Using Thermochemical Water-Splitting Cycles

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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 to create a searchable database with 115 cycles and 822 references. We developed screening criteria to reduce the list to 25 cycles. We used detailed evaluation to select two cycles that appear most promising, the Adiabatic UT-3 cycle and the Sulfur-Iodine cycle. We have selected the Sulfur-Iodine thermochemical water-splitting cycle for further development.

We then assessed the suitability of various nuclear reactor types to the production of hydrogen from water using the Sulfur-Iodine cycle. A basic requirement is to deliver heat to the process interface heat exchanger at temperatures up to 900°C. We considered nine categories of reactors: pressurized water-cooled, boiling water-cooled, organic-cooled, alkali metal-cooled, heavy metal-cooled, gas-cooled, molten salt-cooled, liquid-core and gas-core reactors. We developed requirements and criteria to carry out the assessment, considering design, safety, operational, economic and development issues. This assessment process led to our choice of the helium gas-cooled reactor for coupling to the Sulfur-Iodine cycle.

In continuing work, we are investigating the improvements that have been proposed to the Sulfur-Iodine cycle and will generate an integrated flowsheet describing a hydrogen production plant powered by a high-temperature helium gas-cooled nuclear reactor. This will allow us to size process equipment and calculate hydrogen production efficiency and capital cost, and to estimate the cost of the hydrogen produced as a function of nuclear reactor cost.

I. 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. 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.
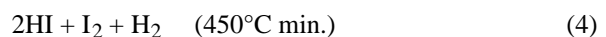
This report describes work during the first phases of a three year project whose objective is to "define an economically feasible concept for production of hydrogen, by nuclear means, using an advanced high-temperature nuclear reactor as the energy source." Thermochemical water-splitting, a chemical process that accomplishes the decomposition of water into hydrogen and oxygen, could meet this objective. The goal of the first phase was to evaluate thermochemical processes which offer the potential for efficient, cost-effective, large-scale production of hydrogen and to select one 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 for hydrogen production.

II. 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.
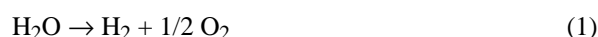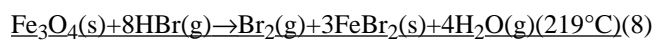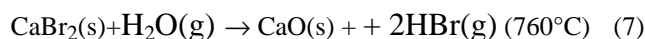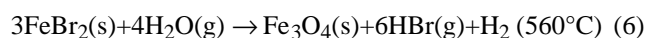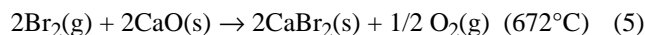
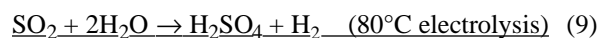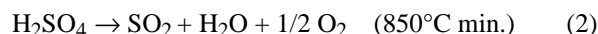$$H_2O \rightarrow H_2 + 1/2 \ O_2 \quad (2500°C \text{ min.}) \qquad (1)$$

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.

$$H_2SO_4 \rightarrow SO_2 + H_2O + 1/2 \ O_2 \quad (850°C \text{ min.}) \qquad (2)$$

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \quad (120°C \text{ min.}) \quad (3)$$

$$\underline{2HI + I_2 + H_2 \quad (450°C \text{ min.})} \qquad (4)$$

$$H_2O \rightarrow H_2 + 1/2 \ O_2 \qquad (1)$$
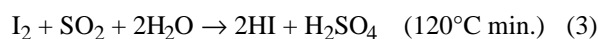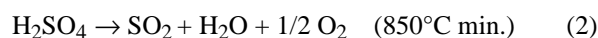
Energy, as heat, is input to a thermochemical cycle via one or more endothermic high-temperature chemical reactions. Heat is rejected via one or more exothermic low temperature reactions. All the reactants, other than water, are regenerated and recycled. In the S-I cycle most of the input heat goes into the dissociation of sulfuric acid. Sulfuric acid and hydrogen iodide are formed in the exothermic reaction of H_2O, SO_2 and I_2, and the hydrogen is generated in the mildly exothermic 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.

$$2Br_2(g) + 2CaO(s) \rightarrow 2CaBr_2(s) + 1/2 \ O_2(g) \quad (672°C) \quad (5)$$

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

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

$$\underline{Fe_3O_4(s) + 8HBr(g) \rightarrow Br_2(g) + 3FeBr_2(s) + 4H_2O(g)(219°C)}(8)$$

$$H_2O \rightarrow H_2 + 1/2 \ O_2 \qquad (1)$$

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.

$$H_2SO_4 \rightarrow SO_2 + H_2O + 1/2 \ O_2 \quad (850°C \text{ min.}) \qquad (2)$$

$$\underline{SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2 \quad (80°C \text{ electrolysis})} \ (9)$$

$$H_2O \rightarrow H_2 + 1/2 \ O_2 \qquad (1)$$

II.A. 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 database program, 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.

We needed a relational database; we selected MS Access 2000. 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.

II.B. Literature Search

The literature survey was designed to locate substantially all thermochemical water-splitting cycles that have been proposed in the open literature. Chemical Abstracts Service of the American Chemical Society provides convenient access to many databases. Various Boolean searches were made 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 I. The databases were subjected to a full data
retrieval search and over 50% of the hits were for papers
related to thermochemical water-splitting. The EndNote
database contains 822 entries, after purging duplicate and
irrelevant entries.

Table I. 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.

II.C. Preliminary Screening

The literature search turned up a large number of
cycles (115), far too many to analyze in depth. It was nec-
essary to establish meaningful and quantifiable screening
criteria and to establish metrics by which each proposed
cycle could be evaluated. The criteria are given in Table II.
Equal weighting was given to each criterion in calculating
the final score. A simple metric could not be devised for
Environmental, Safety and Health (ES&H) concerns. These
were taken into account on a case by case basis after the list
of cycles was limited using the numerical 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 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".
Two cycles were eliminated for ES&H reasons in that they
are based on mercury and we do not believe that it would

Table II. Rational for development of first round screening criteria

	Desirable Characteristic	Rational	Metric
1	Minimum number of chemical reactions steps.	A smaller number indicates a simpler process and lower costs.	Number of chemical reactions.
2	Minimum number of separation steps.	A smaller number indicates a simpler process and lower costs.	Number of chemical separations, excluding simple phase separation.
3	Minimum number of elements.	A smaller number indicates a simpler process and lower costs.	Number of elements, excluding oxygen and hydrogen
4	Employ elements which are abundant.	Use of abundant elements will lower the cost and permit implementation on a large scale.	Score is based on least abundant element in cycle.
5	Minimize use of expensive materials by avoiding corrosive chemicals.	The effect of materials cost on hydrogen production efficiency and cost.	Score is based on the relative corrosiveness of the process solutions.
6	Minimize the flow of solids.	Chemical plant costs are considerably higher for solids processing plants.	Score is based on minimization of solid flow problems.
7	Heat input temperature compatible with materials.	Limit on temperature will be material separating the reactor coolant from the process stream.	Score is based on the high temperature heat input being close to that delivered by an advanced nuclear reactor.
8	Many papers from many authors and institutions.	Cycles that have been thoroughly studied have a lower probability of undiagnosed flaws.	Score is based on the number of papers published dealing with the cycle.
9	Tested at a moderate or large scale,	Processes for which the basic chemistry has not been verified are suspect.	Score is based on the degree to which the chemistry has been actually demonstrated.
10	Good efficiency and cost data available.	A significant amount of engineering design work is necessary to estimate process efficiencies and production costs.	Score is based on the degree to which efficiencies and cost have been estimated.

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 III, along with their scores.

Table III. Reaction details for cycles

Cycle	Name	T/E*	T (°C)	Reaction	Total Score
1	Westinghouse[7]	T	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	85
		E	77	$SO_2(g) + 2H_2O(a) \rightarrow H_2SO_4(a) + H_2(g)$	
2	Ispra Mark 13[8]	T	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	80
		E	77	$2HBr(a) \rightarrow Br_2(a) + H_2(g)$	
		T	77	$Br_2(l) + SO_2(g) + 2H_2O(l) \rightarrow 2HBr(g) + H_2SO_4(a)$	
3	UT-3 Univ. of Tokyo[9]	T	600	$2Br_2(g) + 2CaO \rightarrow 2CaBr_2 + O_2(g)$	79
		T	600	$3FeBr_2 + 4H_2O \rightarrow Fe_3O_4 + 6HBr + H_2(g)$	
		T	750	$CaBr_2 + H_2O \rightarrow CaO + 2HBr$	
		T	300	$Fe_3O_4 + 8HBr \rightarrow Br_2 + 3FeBr_2 + 4H_2O$	
4	Sulfur-Iodine[10]	T	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	78
		T	450	$2HI \rightarrow I_2(g) + H_2(g)$	
		T	120	$I_2 + SO_2(a) + 2H_2O \rightarrow 2HI(a) + H_2SO_4(a)$	
5	Julich Center EOS[11]	T	800	$2Fe_3O_4 + 6FeSO_4 \rightarrow 6Fe_2O_3 + 6SO_2 + O_2(g)$	68
		T	700	$3FeO + H_2O \rightarrow Fe_3O_4 + H_2(g)$	
		T	200	$Fe_2O_3 + SO_2 \rightarrow FeO + FeSO_4$	
6	Tokyo Inst. Tech. Ferrite[12]	T	1000	$2MnFe_2O_4 + 3Na_2CO_3 + H_2O \rightarrow 2Na_3MnFe_2O_6 + 3CO_2(g) + H_2(g)$	64
		T	600	$4Na_3MnFe_2O_6 + 6CO_2(g) \rightarrow 4MnFe_2O_4 + 6Na_2CO_3 + O_2(g)$	
7	Hallett Air Products 1965[11]	T	800	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	62
		E	25	$2HCl \rightarrow Cl_2(g) + H_2(g)$	
8	Gaz de France[11]	T	725	$2K + 2KOH \rightarrow 2K_2O + H_2(g)$	62
		T	825	$2K_2O \rightarrow 2K + K_2O_2$	
		T	125	$2K_2O_2 + 2H_2O \rightarrow 4KOH + O_2(g)$	
9	Nickel Ferrite[13]	T	800	$NiMnFe_4O_6 + 2H_2O \rightarrow NiMnFe_4O_8 + 2H_2(g)$	60
		T	800	$NiMnFe_4O_8 \rightarrow NiMnFe_4O_6 + O_2(g)$	
10	Aachen Univ Julich 1972[11]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	59
		T	170	$2CrCl_2 + 2HCl \rightarrow 2CrCl_3 + H_2(g)$	
		T	800	$2CrCl_3 \rightarrow 2CrCl_2 + Cl_2(g)$	
11	Ispra Mark 1C[14]	T	100	$2CuBr_2 + Ca(OH)_2 \rightarrow 2CuO + 2CaBr_2 + H_2O$	58
		T	900	$4CuO(s) \rightarrow 2Cu_2O(s) + O_2(g)$	
		T	730	$CaBr_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HBr$	
		T	100	$Cu_2O + 4HBr \rightarrow 2CuBr_2 + H_2(g) + H_2O$	
12	LASL- U[11]	T	25	$3CO_2 + U_3O_8 + H_2O \rightarrow 3UO_2CO_3 + H_2(g)$	58
		T	250	$3UO_2CO_3 \rightarrow 3CO_2(g) + 3UO_3$	
		T	700	$6UO_3(s) \rightarrow 2U_3O_8(s) + O_2(g)$	
13	Ispra Mark 8[8]	T	700	$3MnCl_2 + 4H_2O \rightarrow Mn_3O_4 + 6HCl + H_2(g)$	57
		T	900	$3MnO_2 \rightarrow Mn_3O_4 + O_2(g)$	
		T	100	$4HCl + Mn_3O_4 \rightarrow 2MnCl_2(a) + MnO_2 + 2H_2O$	
14	Ispra Mark 6[8]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	56
		T	170	$2CrCl_2 + 2HCl \rightarrow 2CrCl_3 + H_2(g)$	
		T	700	$2CrCl_3 + 2FeCl_2 \rightarrow 2CrCl_2 + 2FeCl_3$	
		T	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	

Table III (continued). Reaction details for cycles

Cycle	Name	T/E*	T (°C)	Reaction	Total Score
15	Ispra Mark 4[8]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	55
		T	100	$2FeCl_2 + 2HCl + S \rightarrow 2FeCl_3 + H_2S$	
		T	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	
		T	800	$H_2S \rightarrow S + H_2(g)$	
16	Ispra Mark 3[8]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	55
		T	170	$2VOCl_2 + 2HCl \rightarrow 2VOCl_3 + H_2(g)$	
		T	200	$2VOCl_3 \rightarrow Cl_2(g) + 2VOCl_2$	
17	Ispra Mark 2 (1972)[8]	T	100	$Na_2O.MnO_2 + H_2O \rightarrow 2NaOH(a) + MnO_2$	55
		T	487	$4MnO_2(s) \rightarrow 2Mn_2O_3(s) + O_2(g)$	
		T	800	$Mn_2O_3 + 4NaOH \rightarrow 2Na_2O.MnO_2 + H_2(g) + H_2O$	
18	Ispra CO/Mn3O4 [14]	T	977	$6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2(g)$	55
		T	700	$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$	
		T	700	$CO(g) + 2Mn_3O_4 \rightarrow C + 3Mn_2O_3$	
19	Ispra Mark 7B[8]	T	1000	$2Fe_2O_3 + 6Cl_2(g) \rightarrow 4FeCl_3 + 3O_2(g)$	54
		T	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	
		T	650	$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2(g)$	
		T	350	$4Fe_3O_4 + O_2(g) \rightarrow 6Fe_2O_3$	
		T	400	$4HCl + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O$	
20	Vanadium Chloride[15]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	53
		T	25	$2HCl + 2VCl_2 \rightarrow 2VCl_3 + H_2(g)$	
		T	700	$2VCl_3 \rightarrow VCl_4 + VCl_2$	
		T	25	$2VCl_4 \rightarrow Cl_2(g) + 2VCl_3$	
21	Ispra Mark 7A[8]	T	420	$2FeCl_3(l) \rightarrow Cl_2(g) + 2FeCl_2$	53
		T	650	$3FeCl_2 + 4H_2O(g) \rightarrow Fe_3O_4 + 6HCl(g) + H_2(g)$	
		T	350	$4Fe_3O_4 + O_2(g) \rightarrow 6Fe_2O_3$	
		T	1000	$6Cl_2(g) + 2Fe_2O_3 \rightarrow 4FeCl_3(g) + 3O_2(g)$	
		T	120	$Fe_2O_3 + 6HCl(a) \rightarrow 2FeCl_3(a) + 3H_2O(l)$	
22	GA Cycle 23[16]	T	800	$H_2S(g) \rightarrow S(g) + H_2(g)$	51
		T	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	
		T	700	$3S + 2H_2O(g) \rightarrow 2H_2S(g) + SO_2(g)$	
		T	25	$3SO_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(a) + S$	
		T	25	$S(g) + O_2(g) \rightarrow SO_2(g)$	
23	US -Chlorine[11]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	50
		T	200	$2CuCl + 2HCl \rightarrow 2CuCl_2 + H_2(g)$	
		T	500	$2CuCl_2 \rightarrow 2CuCl + Cl_2(g)$	
24	Ispra Mark 9[8]	T	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	50
		T	150	$3Cl_2(g) + 2Fe_3O_4 + 12HCl \rightarrow 6FeCl_3 + 6H_2O + O_2(g)$	
		T	650	$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2(g)$	
25	Ispra Mark 6C[8]	T	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	50
		T	170	$2CrCl_2 + 2HCl \rightarrow 2CrCl_3 + H_2(g)$	
		T	700	$2CrCl_3 + 2FeCl_2 \rightarrow 2CrCl_2 + 2FeCl_3$	
		T	500	$2CuCl_2 \rightarrow 2CuCl + Cl_2(g)$	
		T	300	$CuCl + FeCl_3 \rightarrow CuCl_2 + FeCl_2$	

*T = thermochemical, E = electrochemical.

II.D. 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 preliminary block-flow diagrams were made to understand the process complexity. Thermodynamic calculations were made for each chemical reaction over a wide temperature range using HSC Chemistry 4.0.[6] 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 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 1 shows temperature-enthalpy (T-H) curves for three processes matched to the same reactor coolant T-H curve.
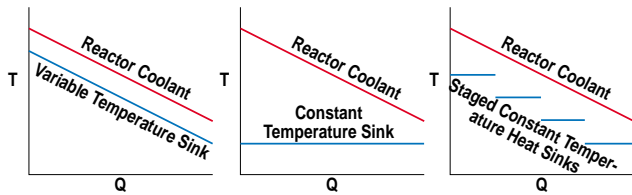

Fig. 1. Matching of thermochemical cycle to reactor.

The first process is well matched as the temperature-enthalpy curves of the process and coolant are parallel. 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.

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.[9] A simplified flow diagram of the Adiabatic UT-3 cycle is shown in Fig. 2. 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.
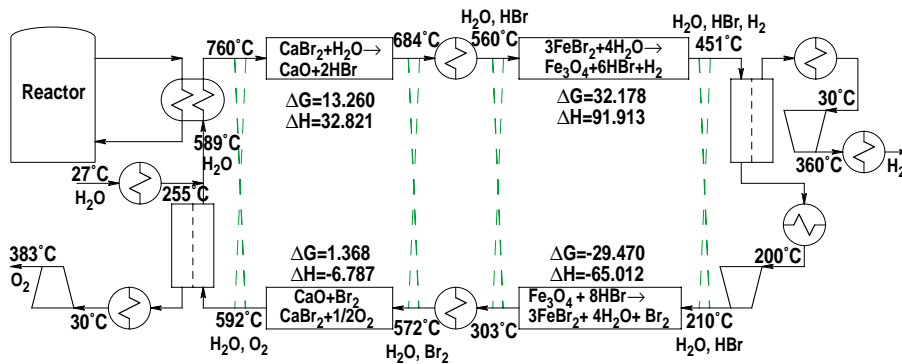

Fig. 2. Adiabatic UT-3 process flow diagram.

The efficiency of hydrogen generation, for a stand-alone plant, is predicted to be 36%-40%. 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 major areas of ongoing research are in the stability of the solids undergoing repeated cycling between the oxide and bromide forms, and in the membrane separation processes.

Sulfur-Iodine Cycle. The Sulfur-Iodine cycle was developed at General Atomics and first described in the mid 1970's.[10] The key to successful implementation of the cycle was using an excess of molten iodine in reaction 3 to give 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. Bench scale experiments were made of the total process and the process was matched to a high-temperature nuclear reactor in 1978 and 1980, with predicted efficiencies of 47% and 52% respectively. The latter flowsheet, however, was optimized solely for maximum efficiency.

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.

The Sulfur-Iodine is the cycle that is almost always used as the standard of comparison as to what can be done with a thermochemical cycle. 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.

III. SELECTION OF NUCLEAR HEAT SOURCE

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
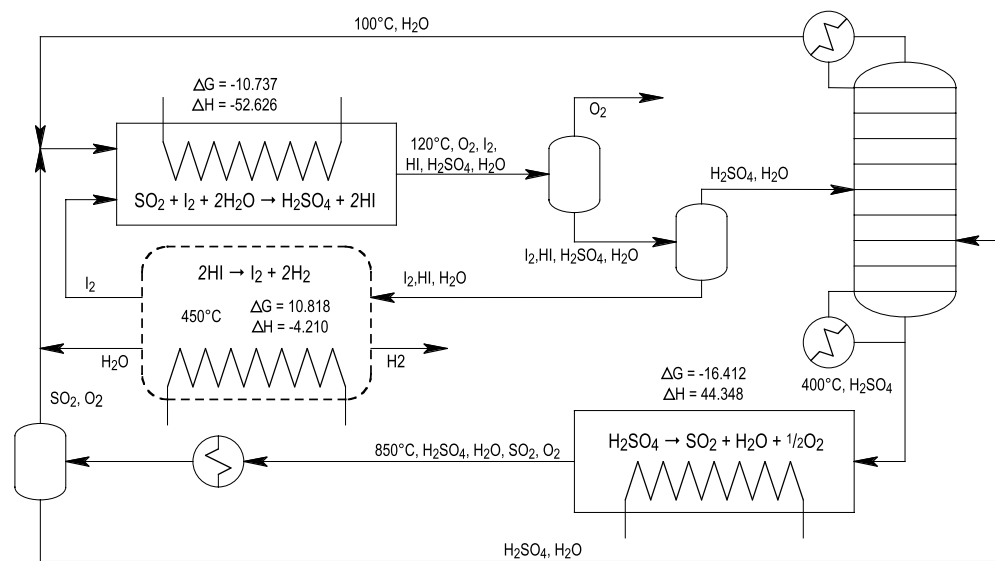

Fig. 3. Sulfur-iodine cycle process flow diagram.

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 reactor outlet temperature of 900°C.

The reactor coolant becomes a primary consideration for determining which concepts are most appropriate. The reactor/coolant types are shown on Table IV and 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 IV. Reactor types considered in the assessment

1. Pressurized Water Reactors[17]
• Pressurized water reactors (light and heavy water)[17,18]
• Supercritical pressurized water reactors[19]
2. Boiling Water Reactors[17]
• Boiling water reactors (light and heavy water)[17]
• Boiling water teactors with duperheat[20,21]
3. Organic-Cooled Reactors[19,20]
• Diphenyl
• Other organic coolants
4. Alkali Liquid Metal-Cooled reactors[17,21]
• Lithium-cooled
• Other (Na, K, NaK)
5. Heavy Liquid Metal-Cooled Reactors[20,22,23]
• Lead-bismuth
• Other (Pb, Bi, Sn, Hg)
6. Gas-Cooled Reactors[19,20,24]
• Noble gasses (He, Ar)
• Other gasses (CO_2, H_2, N_2, air, Ar, steam)
7. Molten Salt-Cooled Reactors[17,18]
• $2LiF\text{-}BeF_2$
• Other salts
8. Liquid-Core Reactors[17,19,20,25]
• Molten salt-core
• Liquid metal-core
• Aqueous-core
9. Gas-Core Reactors[26]
• 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 be 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 V. 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 V. Requirements and important criteria

Basic Requirements
1. Chemical compatibility of coolant with primary loop materials and fuel.
2. Coolant molecular stability at operating temperatures in a radiation environment.
3. Pressure requirements for primary loop.
4. Nuclear requirements: parasitic neutron capture, neutron activation, fission product effects, gas buildup, etc.
5. Basic feasibility, general development requirements, and development risk
Important Criteria
1. Safety
2. Operational issues
3. Capital costs
4. Intermediate loop compatibility
5. Other merits and issues

III.A. Status and Characteristics of Reactor Types

Gas-core reactors were considered too speculative to be seriously considered for hydrogen production and were eliminated. 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 VI. Pressurized water and boiling water

Table VI. Reactor coolant basic properties

Coolant	Density[a] (g/cc)	σ_{th} Parasitic (b)	Neutron Activation	Radiolytic Decomposition	Hazards Toxic	Hazards Fire	Hazards Explos.	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure (MPa)[b]	Heat Transport Properties	Thermal Stability Limit (K)	Chemical Attack at 900°C
Water													
H$_2$O	1	0.66	Some	Some	No	No	No	0	100	13.7	Very good	Stable	Yes
D$_2$O	1.1	0.001	Some	Some	No	No	No	0	101	13.7	Very good	Stable	Yes
Organic													
Diphenyl	0.86	0.33	low	Yes	No	No	No	69	255	0.2	Good	750	Yes
Alkali Metal													
Li	0.53	71	High	Stable	Yes	Yes	Yes	181	1331	10^{-10}	Excellent	Stable	Yes[c]
Na	0.82	0.525	High	Stable	Yes	Yes	Yes	98	881	5×10^{-6}	Excellent	Stable	Yes[c]
NaK	0.74	0.5	High	Stable	Yes	Yes	Yes	-11	784	$\sim10^{-4}$	Excellent	Stable	Yes[c]
K	0.70	2.07	High	Stable	Yes	Yes	Yes	64	761	10^{-4}	Excellent	Stable	Yes[c]
Heavy Metal													
Sn	6.5	0.625	High	Stable	No	No	No	232	2270	$<10^{-14}$	Excellent	Stable	Some[d]
Hg	13.6	380	High	Stable	High	No	No	-38.5	358	0.07	Excellent	Stable	Some[d]
Pb	11.4	0.17	High	Stable	Yes	No	No	327	1840	10^{-13}	Excellent	Stable	Some[d]
Bi	9.75	0.034	High	Stable	No	No	No	271	1570	10^{-11}	Excellent	Stable	Some[d]
PbBi	~10	~0.1	High	Stable	Yes	No	No	125	1670	10^{-11}	Excellent	Stable	Some[d]
Gases													
H$_2$	0.00009	0.332	Low	Stable	No	High	High	—	—	—	Poor	Stable	Yes
He	0.00018	0.007	No	Stable	No	No	No	—	—	—	Poor	Stable	No
N$_2$	0.0013	1.88	No	Stable	No	No	No	—	—	—	Poor	Stable	Yes
Ar	0.0018	0.66	Yes	Stable	No	No	No	—	—	—	Poor	Stable	No
CO$_2$	0.0015	0.0038	Some		No	No	No	—	—	—	Poor	<850	Yes
Air	0.0013	~1.3	Yes		No	No	No	—	—	—	Poor	<850	Yes
Steam	0.00056	0.66	Some	Some	No	No	No	0	100	—	Poor	—	High
Molten Salt													
2LiF-BeF$_2$	~2	-	Yes	Stable	Yes	No	No	457	1397	$<10^{-9}$	Excellent	Stable	Yes
Liquid Core													
Aqueous	~1	-	Fission products Very high	Some	Yes	No	No	—	—	~10	Excellent	Some fuel precipitation	Yes
Liquid metal	~10	-		Stable	Yes	Yes	Yes	~300	~1500	Low	Excellent	Some fuel precipitation	Yes
Molten salt	~2.5	-		Stable	Yes	No	No	497		$>10^{-9}$	Excellent	Stable ?	Yes

[a] At ambient temperature.　[b] At saturation 600 K.　[c] Nb alloys may be suitable.　[d] Coolant additives may be suitable.

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.

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

Grading Basis for Requirements
A— Projected or demonstrated feasible
B— Promising, but development needed
C— Possible, needs significant development
F— Not feasible (eliminate from consideration)

Grading Basis for Criteria
A— Ideal
B— Good, not optimum
C— Issues or poorly suited, but possible
F— Unacceptable (eliminate from consideration)

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 was used to select a baseline concept. 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 needed development activities were identified and evaluated:

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 VIII, which shows that the GCR appears to result in the lowest development cost and risk.

III.B. 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.
- Liquid-core and alkali metal-cooled reactors – significant development risk.
- Heavy metal and molten salt-cooled reactors – promising.
- Gas cooled reactors – baseline choice.

Table VII. 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

Table VIII. Assessment of reactor concepts for use with the Sulfur-Iodine thermochemical cycle

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

Helium gas-cooled reactors are recommended as the baseline choice for a reactor heat source for a Sulfur-Iodine thermochemical cycle for hydrogen production.

IV. 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 822 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 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 requirements and 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 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.

We will define equipment specifications for the chemical process equipment that will form the basis for the cost estimates, to be made using standard chemical engineering techniques based on process equipment sizes and materials. The result of this work will be an evaluation of the process efficiency and an estimate of the cost of hydrogen. We will then be able to recommend the steps necessary to bring the process to the point of commercialization.

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