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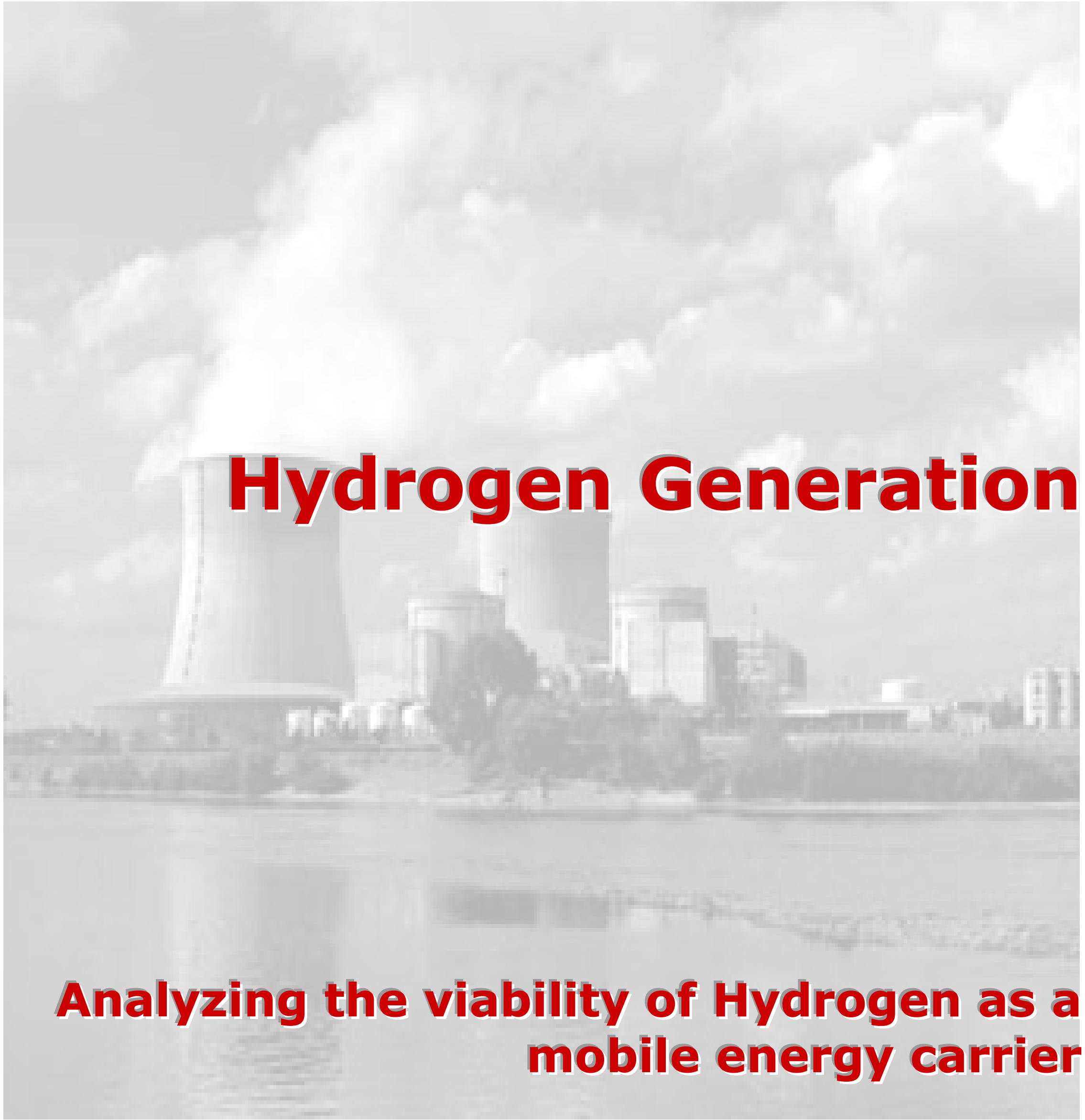

Hydrogen Generation

Analyzing the viability of Hydrogen as a mobile energy carrier

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Executive Summary

In many scientific circles, the discussion of Hydrogen production for the storage and transportation of energy is a main topic. Hydrogen is a promising energy carrier, which potentially could replace the fossil fuels used in the transportation sector of our economy. Fossil fuels are a limited resource and are mass polluters with carbon dioxide emission from their combustion holding the main responsibility for global warming.

As fossil fuel supplies decrease and oil prices increase, the transportation industry will begin to be more accepting of alternative energy sources. If a cheap, reliable method of hydrogen production is secured, hydrogen will offer the viable alternative that is sought.

Hydrogen can be produced through steam reforming or water splitting cycle. A water splitting cycle is a combination of water and heat that are fed through a series of reactions in a cycle, producing the basic elements along with waste heat. However, this method is currently more capital intensive then the steam reforming and has a higher production cost.

In this report a thermodynamic analysis of each cycle was performed, using a heat cascade, equilibrium constants and free energy of reactions. From this, the cycle efficiency was determined.

The cycle with the greatest heat cascade efficiency was the Hallett Air Products with 99.7%. A plant capable to produce 500 tonnes of hydrogen per day will be constructed and located at Hartsville, South Carolina. This is based on the knowledge that Duke Energy is constructing a new nuclear power plant using a Gas Turbine Modular Helium Reactor. The plant is scheduled to operate in 2015. The hydrogen production plant would service three major cities: Columbia, S.C., Raleigh, N.C., and Charlotte, N.C. These cities have a combined population of 965,166. Our team has used this value to aid in the calculations for production, transporting, and storing hydrogen for those cities. Our team's economic market for hydrogen is Hydrogen Fuel Cell (HFC) cars.

The total capital investment for the Hallett Air cycle required for the hydrogen plant, distribution piping, and storage facilities is **1.1 billion USD**. The energy costs would be 14 kWh (t)/kg of H_2 produced or 38.7 kWh (e)/kg. Using this process, the cost of Hydrogen to be **\$2.30/kg** with a selling price of \$4.75/kg of H_2. The investor's rate of return for this process is 10.28% with a NPV of \$30,605,100. Comparing this to the Sulfur-Iodine process at the same location, would require a total capital investment of **1.5 billion USD**. The energy costs would be 75.7 kWh (t)/kg of H_2 produced. The resulting cost of Hydrogen would be **\$1.97/kg** with a selling price of \$4.75/kg of H_2. The selling price of hydrogen included the depreciation of the production plant. The investor's rate of return for this process is 8.26% with a NPV of -\$247,152,500. These costs are based on the safe investment assumption of 10% and depreciation is factored. Furthermore, the costs do not include the capital cost of a new nuclear power plant.

Chapter 1: Introduction

1.0 Introduction

Thermochemical cycles produce hydrogen by a series of chemical reactions where the net result is the decomposition or splitting of water, $H_2O \rightarrow H_2 + \frac{1}{2} O_2$, at much lower temperatures than can be done with heat alone. When water decomposes at temperatures above 2,500°C, it is called thermolysis.

A pure thermochemical cycle involves a series of chemical reactions that are driven only by thermal energy. The net result of the input of heat and water is hydrogen and oxygen production. All other process chemicals in these systems are fully recycled. Hybrid thermochemical cycles include both chemical reaction steps and an electrolysis step of some chemical compound (not water) that usually produces hydrogen. Both thermal and electrical energy is required to complete the hybrid cycle. However, the energy requirements for the electrolysis step are much less than for electrolysis of water.

The temperatures required to drive the endothermic reactions for most thermochemical cycles are challenging – generally in the 750 to 1000°C range or higher. Thermochemical cycles are considered promising options for hydrogen production because of the potential for high efficiencies and scaling to large capacities. Thermochemical cycles are generally considered to have potential for lower costs than conventional electrolysis of water because the production of hydrogen by electrolysis requires conversion of heat to electricity prior to hydrogen production, whereas thermochemical cycles produce hydrogen directly from thermal energy. Finally, the status of thermochemical cycle technology is relatively immature, but there is a greater potential for improvement compared with conventional electrolysis.

Currently 86% of the world's energy is produced from fossil fuels. This is resulting in the release of CO_2 gas, which is causing climate changes and contributing to global warming from the quantities currently produced. Currently less than 50% of the known oil reserves have been used, but the costs in procuring this source of energy are increasing significantly, allowing a renewable energy source to enter the market where ultimately, such a sustainable energy source will be required.

Hydrogen can be used in very efficient fuel cells to produce electricity and water. If the hydrogen is supplied by splitting water, it completes a cycle in which no byproducts are produced. The problem with this process is that thermodynamics proves that at the very least the energy necessary to split the water is equal to the amount of energy provided by using the hydrogen in a fuel cell.

Steam reforming is the current large scale and cost effective method for hydrogen production. However, steam reforming depends on natural gas, which will require more money to obtain as it becomes more scarce. In addition, steam reforming of natural gas produces carbon dioxide, which causes concern for climate change.

"When hydrogen is produced using energy derived from fossil fuels, there is little or no environmental advantage"[1]. Thus for hydrogen to be an effective replacement for fossil fuels it need to be produced without the consumption of fossil fuels.

Some of this energy can come from direct solar energy or indirect solar energy (hydroelectric, wave, wind). These energy sources are difficult to use and will not produce the amount of energy required. Therefore, the heat supplied by nuclear fission would be the best energy source. When considered in conjunction with nuclear power, hydrogen powered cells are a very realistic advancement both environmentally and economically.

1.0.1 Objective

The objective of the thermochemical cycle research is to develop and demonstrate thermochemical processes to produce hydrogen cost effectively using nuclear energy.

1.1 Research Progress

A thorough literature search was performed to locate all thermochemical water splitting cycles. The cycles located were screened using objective criteria, to determine which can benefit, in terms of efficiency and cost, from the high temperature capabilities of advanced nuclear reactors. The literature search generated too many cycles to analyze in depth. In order to launch an objective screening criterion, with which to reduce the number of cycles to a manageable number, it was necessary to establish meaningful criteria. The desirable cycle characteristics upon which quantifiable metrics were developed and used as screening criteria are as follows:

- Have a minimum number of chemical reaction steps in the cycle.
- Have a minimum number of separation steps in the cycle.
- Have a minimum number of elements in the cycle.
- Have good efficiency and cost data available.
- Have been the subject of many papers from many authors and institutions.

As part of the screening process, detailed investigations were made into the capability of each cycle. The most recent papers were obtained for each cycle, thermodynamic calculations were made over a wide temperature range, and each chemical species was considered in each of its potential forms (gas, liquid, solid, and aqueous solution). Because of this analysis, three cycles were rated far above the others: Sulfur-Iodine, University of Tokyo Cycle 3 (UT-3), and the Modified UT-3 cycle.

Chapter 2: Power Sources

2.0 Introduction

At the start of the 21st century, most of the electricity consumed in the U.S. and the burning of fossil fuels is still generating the rest of the world. Even larger quantities of fossil fuels are being burned to meet other demands imposed by the residential, commercial, industrial, and transportation sectors. In 1999, the U.S. imported 58% of its crude oil and 37% of its total energy supply, and burning fossil fuels in the U.S. resulted in the emission of 11.3 million metric tons of sulfur dioxide, 4.9 million metric tons of nitrogen oxide, and an astounding 1510 million metric tons of carbon dioxide. It is clear that a new energy policy must address these environmental, economic, and energy-security concerns. With recent technological advances, a strong case can be made to include nuclear energy as a major component of a 21st-century energy policy. First, other renewable energy sources and their disadvantages for use will be discussed.

2.1 Solar Power

The idea of cultivating the sun and wind as sources of energy for humanity is attractive. It appeals to the sense of "being one with nature." Sun and wind are clean; there is no mess or pollutants, and they do not appear to be dangerous. The problem is not with technology, but with the laws of physics itself. Solar power comes to the earth from the sun at a rate of 1 kW/m^2. An example of how weak this power is, to heat one sizable swimming pool with solar power, one would need a set of collectors spread out over the roof of a house or lawn.

A 1,000 MWe power plant will be used as a comparison for solar, wind, and nuclear energy. This is a typical size used today to produce electricity. A nuclear power plant would need about 25 acres for the plant itself plus storage facilities, rail yards, etc. A solar plant producing the same amount of power (with 10% efficiency and 50% spacing between collectors) would need 50 square miles. Since the sun is not out at night or if there are cloudy days, the plant would have to be designed for a greater capacity, enabling its storage facilities to supply an average of 750 MW when the collectors are ineffective. The disadvantages of solar is that the input is interrupted by night and cloud cover, electric generation has a low capacity factor, typically less than 15%, the collectors are expensive to make, the materials are environmental concern: crystalline silicon and gallium arsenide. Solar power derived from sun is not economically feasible or practical to aid in the production of hydrogen.

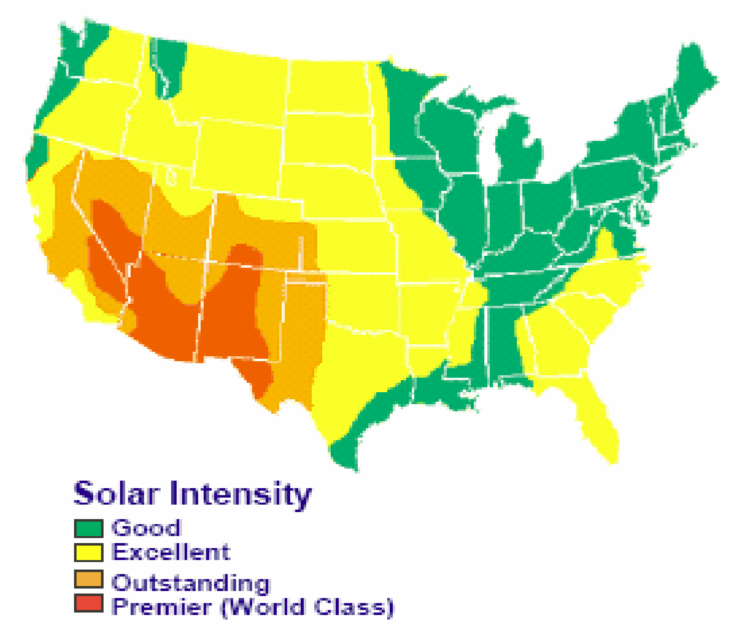


Figure 1 Map of Solar Intensity of the United States

2.2 Wind Power

Wind energy is an indirect form of solar energy. It is estimated that 1-2% of the solar radiation that reaches the earth is converted to wind energy. In general, wind results from an unequal heating of different parts of the earth, causing cooler, dense air to circulate to replace warmer light air. While some of the sun's energy is absorbed directly by the air, most of the energy in the wind is first absorbed by the surface of the earth and then transferred to the air by convection.

Wind energy is recognized worldwide as a proven technology to meet increasing electricity demands in a sustainable and clean way. Offshore wind energy has the added attraction that it has minimal environmental effects. Moreover, higher wind speeds at sea mean an increased energy production, as energy output is a function of the cube of the wind speed. Average offshore wind energy increase ranges from 10-20%.

It is expected that an important part of the future expansion of wind energy utilization at least in Europe will come from offshore sites. The first large offshore wind farms are currently in the planning phase in several countries in Europe. However, the economic viability of offshore wind farms depends on the favorable wind conditions compared to sites on land. The higher energy yield has to compensate the additional installation and maintenance cost. For project planning, especially for large projects, a reliable prediction of the wind resource is therefore crucial. While the global wind-generation market is growing at 28% annually, it relies overwhelmingly on government subsidies.

2.2.1 Environmental Impacts of Wind Power

The environmental impact of offshore wind farms is considerably reduced compared with those onshore; both noise and visual impact are unlikely to be issues, but there are still some considerations. For example, there could be an environmental impact from working offshore, such as localized disturbance of the seabed.

2.2.2 Costs of Wind Power

Current cost estimates are based partly on European experience since 1991. They indicate offshore wind energy costs fewer than 6 cents per kWh. Capital costs are around 30-50% higher than onshore, due to larger machine size and the costs of transporting and installing at sea. This is partially offset by higher energy yields - as much as 30%. However, as happened onshore, these prices are expected to drop as technology improves and more experience is gained. Wind resources up to 40 kilometers from shore are currently considered economically feasible according to studies in Denmark, with the key factor being water depth.

Most developments will be either installed on gravity foundations or sited on steel monopiles. Gravity foundations are concrete structures that are stabilized by sand or water and the turbine tower fits into them. Monopiles are long, steel tubes, which are hammered, drilled or vibrated into the seabed until secure, and then platforms and towers are installed on top. Although it would be technically feasible to mount wind turbines on floating structures, studies have shown that it would be very expensive to do this.

2.2.3 Disadvantages of Wind Power

Wind is not predictable so other forms of power must be available to make up any shortfall. The cost of electricity is a major factor in hydrogen production costs. Although any solar energy option can generate the electricity needed for hydrogen production, the cost of electricity generated from photovoltaic solar cells is approximately 10-times more expensive than the electricity generated from megawatt-scale wind machines. Wind systems, which have an installed capital cost of approximately $1,000 per kW and a 35% capacity factor, are able to generate electricity for approximately 4-cents per kWh.

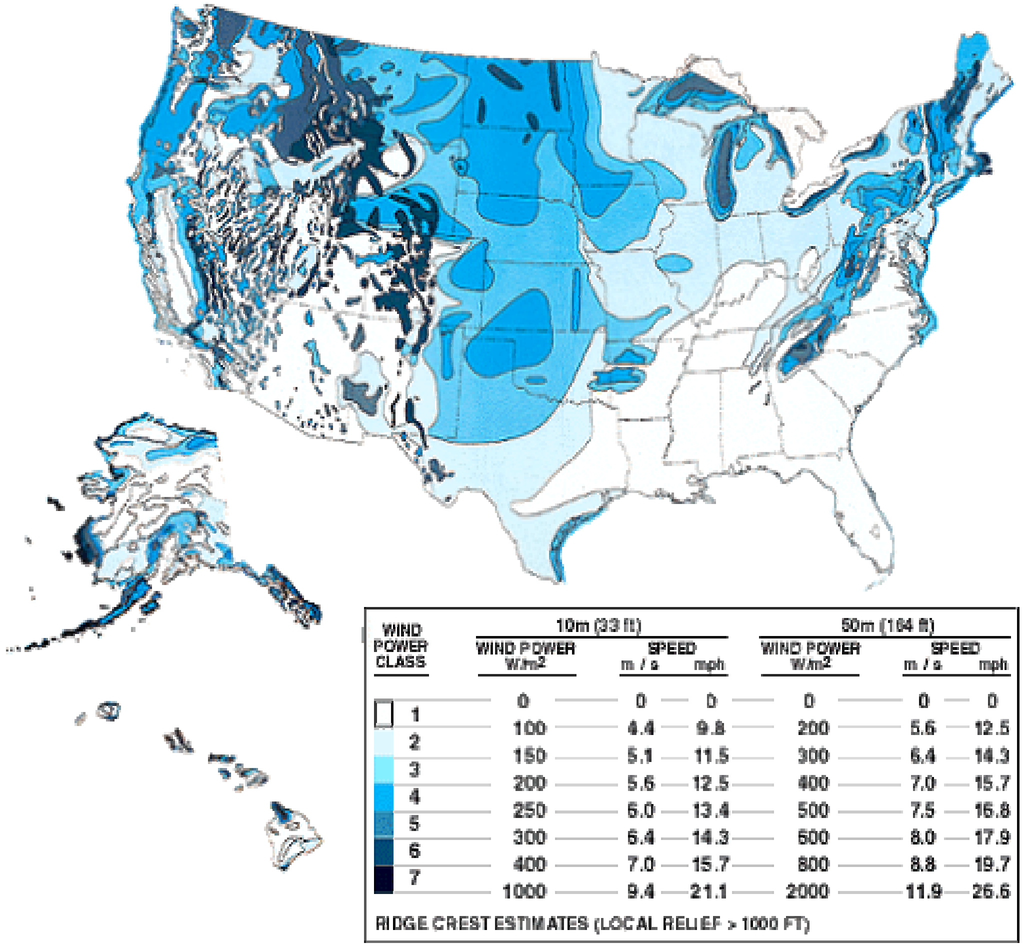


Figure 2 Map of Wind Intensity of the United States

2.3 Nuclear Power

Nuclear energy is an attractive potential source of hydrogen for the Hydrogen Economy. A large hydrogen market already exists and it is growing rapidly to provide increasing amounts of hydrogen to oil refineries for upgrading heavy crude oils and producing clean-burning products. This market is expected to continue growing at ~10%/yr, doubling by 2010 and doubling again by 2020. To transition to a "Hydrogen Economy" would take still more hydrogen. The recent DOE-supported study of nuclear production of hydrogen identified the Sulphur-Iodine thermochemical water splitting cycle coupled to the Modular Helium Reactor (the GT-MHR) as an attractive candidate system for hydrogen production.

2.3.1 Factors Favoring Uranium

Uranium has the advantage of being a highly concentrated source of energy that is easily and cheaply transportable. The quantities needed are very much less than for coal or oil. One kilogram of natural uranium will yield about 20,000 times as much energy as the same amount of coal. It is therefore intrinsically a very portable and tradable commodity. The fuel's contribution to the overall cost of the electricity produced is relatively small, so even a large fuel price escalation will have relatively little effect. For instance, a doubling of the 2002 U_3O_8 price would increase the fuel cost for a light water reactor by 30% and the electricity cost about 7% (whereas doubling the gas price would add 70% to the price of electricity).

2.3.2 Energy Production Rates

Uranium-235 is the isotope of uranium used in nuclear reactors. Uranium-235 can produce 3.7 million times as much energy as the same amount of coal. As an example, seven trucks, each carrying 6 cases of 2-12 foot high fuel assemblies, can fuel a 1000 MWe reactor for 1.5 years. To operate a coal plant of the same output would require 1 train of 89-100 ton coal cars **EVERY** day. Over 350,000 tons of ash would be produced and over 4 million tons of carbon dioxide, carbon monoxide, nitrogen oxides and sulfur oxides would be released to the environment.[2]

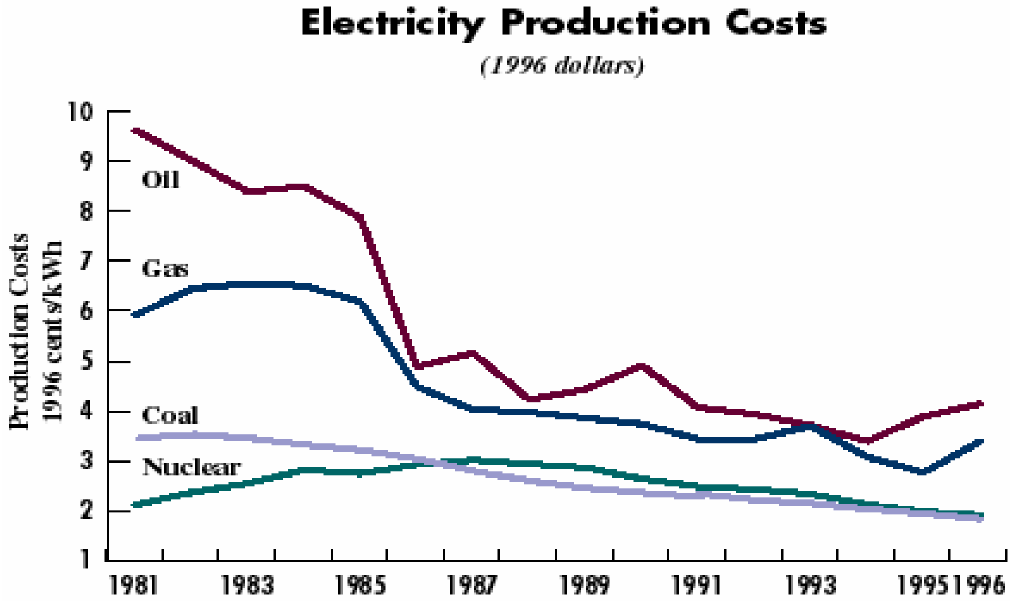


Figure 3 Electricity Production Costs of Energy Sources[3]

Estimated costs show that hydrogen production by the GT-MHR could be competitive with current techniques of hydrogen production from fossil fuels if CO_2 capture and sequestration is required. This favorable situation is expected to improve as the cost of natural gas rises. Nuclear production of hydrogen would allow large-scale production of hydrogen at economic prices while avoiding the release of CO_2. Nuclear production of hydrogen could thus become the enabling technology for the Hydrogen Economy.

The Gas Turbine–Modular Helium Reactor (GT-MHR) is an advanced nuclear power system that offers unparalleled safety, high thermal efficiency, high proliferation resistance, low environmental impact, waste management benefits and competitive electricity generation costs.

2.4 Concept of Design

The GT-MHR combines a meltdown-proof reactor and advanced gas turbine technology in a power plant with improvement in thermal efficiency approaching 50%. This efficiency makes possible much lower power costs, without the environmental degradation and resource depletion of burning fossil fuels.

The GT-MHR has high application flexibility because the high outlet temperature of the MHR reactor can be utilized to provide high heat energy for applications other than to produce electricity. A current application having high potential for a demonstration project in the US is coupling of the MHR with a Sulphur-Iodine (S-I) thermochemical water-splitting process to produce hydrogen. The S-I cycle (Figure 9) consists of three chemical reactions, which sum to dissociation of water. Only water and high temperature process heat are input to the cycle and only hydrogen, oxygen and low temperature heat are output. All the chemical reagents are regenerated and recycled; there are no effluents. An intermediate helium heat transfer loop would be used between the MHR coolant loop and the hydrogen production system. At the standard MHR outlet temperature of 850°C, a maximum temperature of 825°C is estimated for the heat to the process, which yields

43% efficiency. At a reactor outlet temperature of 950°C and a 50ºC temperature drop across an intermediate heat exchanger, an efficiency of 52% is estimated.[4]

An alternative hydrogen production process using high temperature process heat from the MHR is high temperature electrolysis. In this process, some of the energy would be used as electricity and some used directly as heat. Hydrogen production efficiencies of about 50% at 900°C are theoretically achievable with this process.

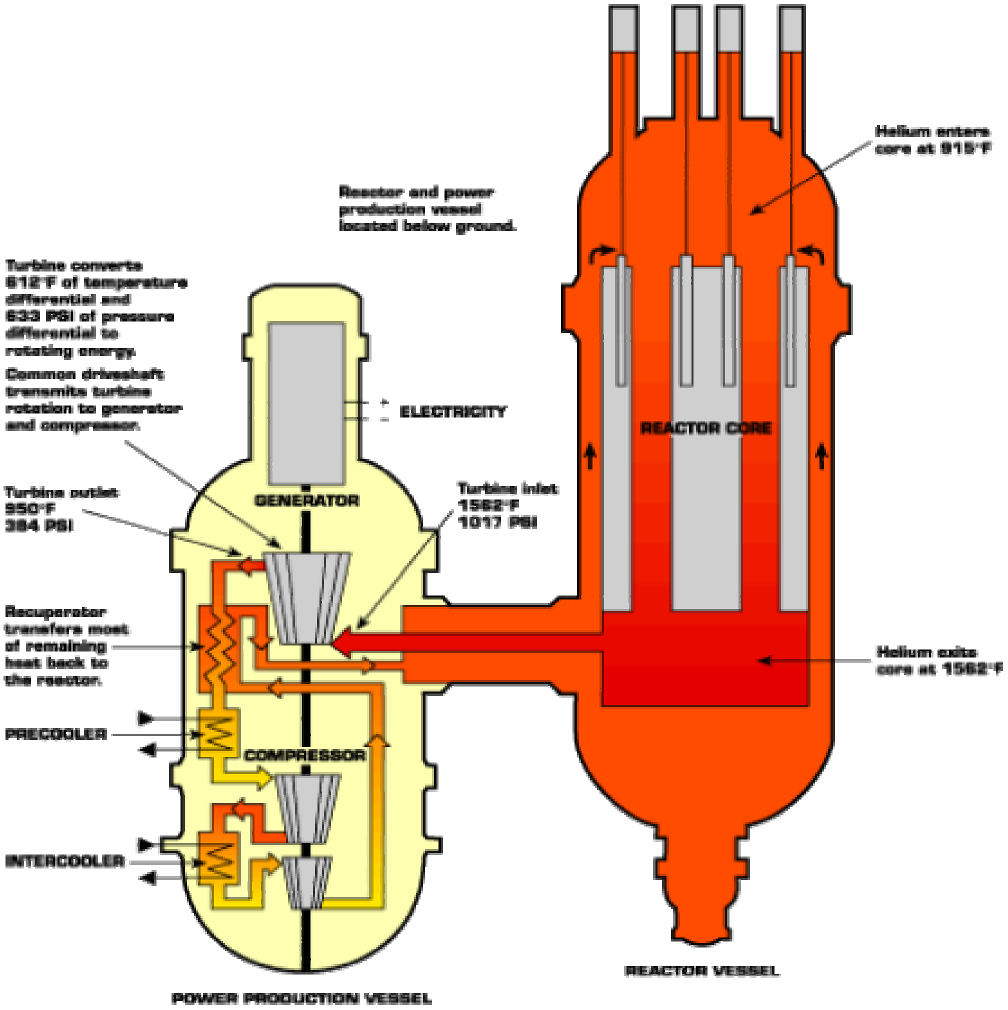


Figure 4 Schematic Flow Diagram of a Gas Turbine Modular Helium Reactor[5]

The entire GT-MHR power plant is contained in two interconnected pressure vessels enclosed within a below-ground concrete containment structure. One vessel contains the reactor system and is based on the steam-cycle MHR and the second vessel contains the entire power conversion system. The turbo-machine consists of a generator, turbine and two compressor sections mounted on a single shaft rotating on magnetic bearings. The active magnetic bearings control shaft stability while eliminating the need for lubricants within the primary system. The vessel also contains three compact heat exchangers. The most important of these is a 95% effective recuperator, which recovers turbine exhaust heat and boosts plant efficiency from 34% to 48%.

Chapter 3: Hydrogen Transportation

3.0 Infrastructure

Pipeline transmission is the most economical method of transporting hydrogen in large quantities from generation to point-of-use. Due to hydrogen's relatively low volumetric energy density, transportation and final delivery to the point of use can be one of the significant costs and energy inefficiencies associated with using hydrogen as an energy carrier. DOE is developing hydrogen fuel delivery technologies that enable the introduction and long-term viability of hydrogen as an energy carrier for transportation and stationary power.

3.1 Transport of Hydrogen[6]

3.1.1 Location of Hydrogen Plant

The location of the hydrogen production plant was because Duke Energy is in the process of looking into locations in North and South Carolina for a new nuclear power plant. One area they are interested in is Hartsville, South Carolina[7]. This new nuclear power plant would consist of a Generation IV reactor: Gas Turbine Modular Helium Reactor designed by General Atomics. Below is a map of the location of Hartsville, South Carolina and referencing three major cities that is nearest.

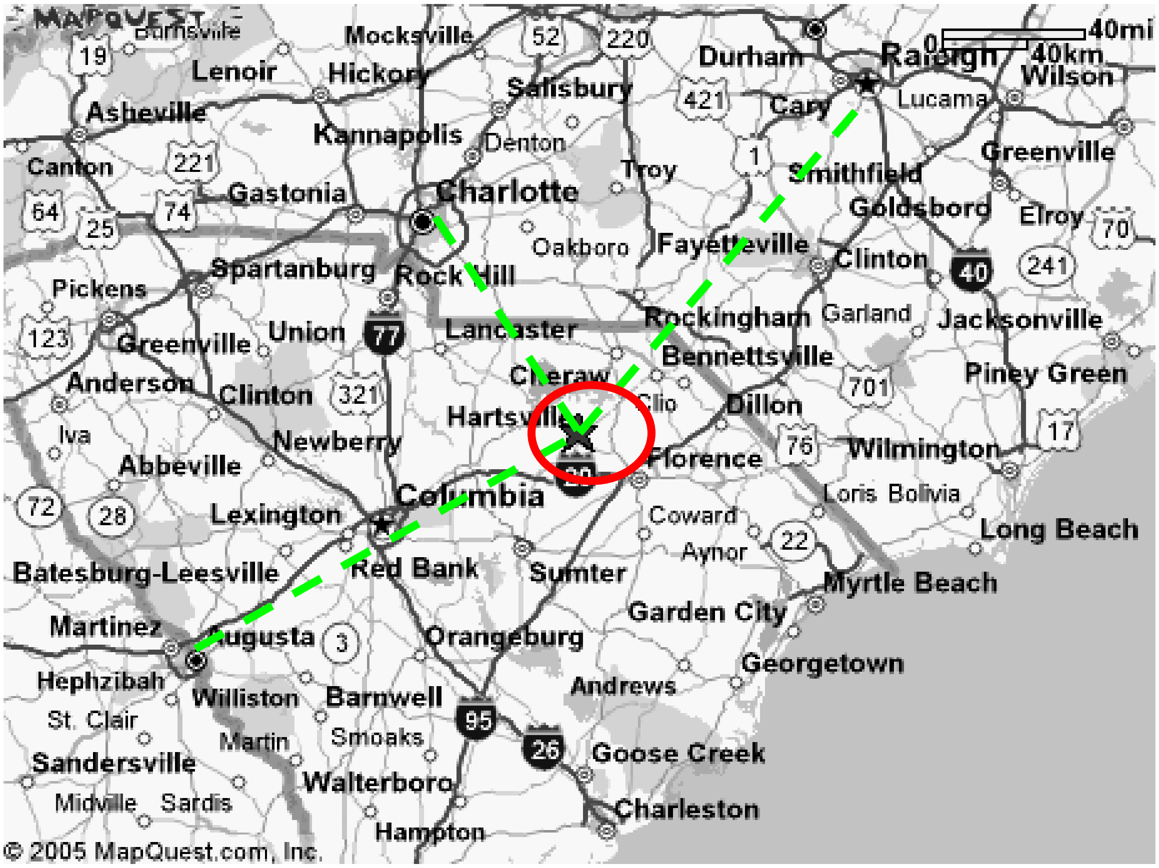


Figure 5 Map of Hartsville, South Carolina. Location of new H_2 Production Plant

3.1.2 Pipelines

In the United States, there is 720 km of hydrogen pipeline network. Over great distances, pipeline transport of hydrogen could be an effective way of transporting energy. Hydrogen pipes that are in use today are constructed of regular steel pipe, and operate under pressures of 10-20 bar (145-290 psi), with a diameter of 25-30 cm (~10"-12"). If the speed is increased by a factor of 2.8 to compensate for hydrogen having 2.8 times lower energy density per volume than natural gas, the same amount of energy can be moved. The fact is that by using efficient hydrogen technology such as fuel cells, etc., the same amount of transported energy will yield increased output at final consumption. In the natural gas distribution network, pressure is low, around 4 bar, and so cheaper plastic pipe is usually used. PVC (Poly Vinyl Chloride) and the newer HDPE (High Density Poly Ethylene) are too porous and not usable for transporting hydrogen.

Gas pipelines used for transportation can store great quantities of hydrogen. By regulating the pressure in the pipes, it is possible to use the large volume a pipeline offers as storage during peak situations.

The natural gas distribution system includes 2,785,000 km (1,730,000 mi) of relatively small-diameter, low-pressure piping, which is divided into 1,739,000 km (1,080,000 mi) of distribution main and 1,046,000 km (650,000 mi) of services. There are approximately 55 million services in the distribution system. The typical distribution of piping diameters is between 40 mm and 150 mm (1.5 in and 6 in) for main distribution piping and 13 mm to 20 mm (0.5 in to 0.75 in) for service piping. A small percentage of distribution mains and services have a larger diameter pipe, typically for commercial and industrial application.

Now with this in mind, the costs to provide a hydrogen distribution system with the same magnitude would have astronomical costs. To have a distribution infrastructure established of 420 km for the three cities from Hartsville, S.C. would cost **$3.4 million**. This is the cost for a 12” Type 304 stainless steel pipe at $800/m.

H_2 Piping

Information	Data	Results
Diameter of Pipe (m)	0.3048	
Material of Pipe	Type 304 Stainless Steel	
Cost of Material ($/m)	**$800**	
Length of Pipe Needed (km)		
From **Hartsville** to		
Columbia	97.8	$78,278,480
Charlotte, NC	118.1	$94,500,640
Raleigh, NC	203.3	$162,608,080
Augusta, GA	202.3	$161,835,600
Winstom-Salem, NC	192.8	$154,239,520

Table 1 Hydrogen Pipeline Delivery Costs to Surrounding Cities fro Hartsville, S.C.

The following table shows the distances from our hydrogen production plant in Hartsville, South Carolina to the closet major cities with their respective costs of transmission pipelines.

From **Hartsville** to	**Miles**	**Kilometers**			**Population**
Charlotte, NC	73.38	118.1	$94,480,000		540,828
Raleigh, NC	126.32	203.3	$162,640,000		306,944
Columbia, SC	60.77	97.8	$78,240,000		117,394
Total	260.48	**419.20**		**$335,360,000**	**965,166**
Augusta, GA		202.3	$161,840,000		193,101
Winston-Salem, NC		192.8	$154,240,000		188,934

Table 2 Distances from Hartsville to closet major cities

3.1.3 Transport of Liquid Hydrogen

Liquid hydrogen (LH_2) is hydrogen cooled below -253ºC. The cooling process requires a great deal of energy, but for long-distance transportation and as fuel in certain applications used in air and space travel, LH_2 still has obvious advantages over other fuels.

3.1.4 Roadway Transportation

Hydrogen shipped with tank trucks in both liquid and compressed states. Several companies currently deliver these types of tank trucks. The number of tube trailers needed to transport hydrogen to the three major cities from Hartsville, S.C., is shown in Appendix 10.2, Table 9, giving 2500 trailers.

3.1.5 Ocean Transportation

Hydrogen transported as a liquid in tank ships are not too different from LNG tankers, aside from the fact that better insulation is required to keep the hydrogen cooled down over long distances. The Japanese WE-NET and the German-Canadian Euro Quebec have reported on the use of such tanks. The evaporated hydrogen may be used as fuel onboard. In 1990, the German institute for materials research declared that LH_2 could be given the same safety rating as LPG and LNG, and transport of LH_2 into German harbors was approved.

3.1.6 Air Transportation

There are several advantages in transporting LH_2 by air rather than by ship. LH_2 is lightweight and the delivery time is much shorter, and evaporation is therefore not a big problem. Studies on this have been done by CDS Research Ltd. in Canada, with support from the WE-NET program.

Chapter 4: Hydrogen Market

4.0 Market Environment

Hydrogen must be packaged, transported, stored and transferred, to bring it from production to final use. This requires energy. In today's fossil energy economy, the energy lost between the well and the consumer is about 12% for oil and about 5% for gas.

Considerable amounts of hydrogen are generated, handled, transported and used in the chemical industry today. However, this hydrogen is a chemical substance, not an energy commodity. Hydrogen production and transportation costs are absorbed in the price of the synthesized chemicals. The cost of hydrogen is irrelevant as long as the final products find markets. The use of hydrogen is dictated by economic arguments and not by energetic considerations.

If hydrogen is to be used as an energy carrier, how much energy is required to make, package, handle, store and transport hydrogen? It would be difficult to establish a sustainable energy future if much of the energy harvested is wasted before it reaches the consumer.[8]

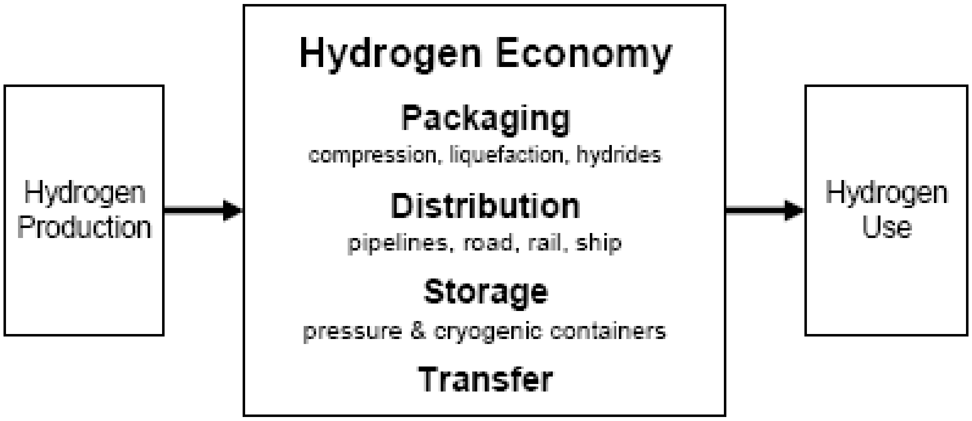


Figure 6 Schematic Representation of an elemental "Hydrogen Economy"

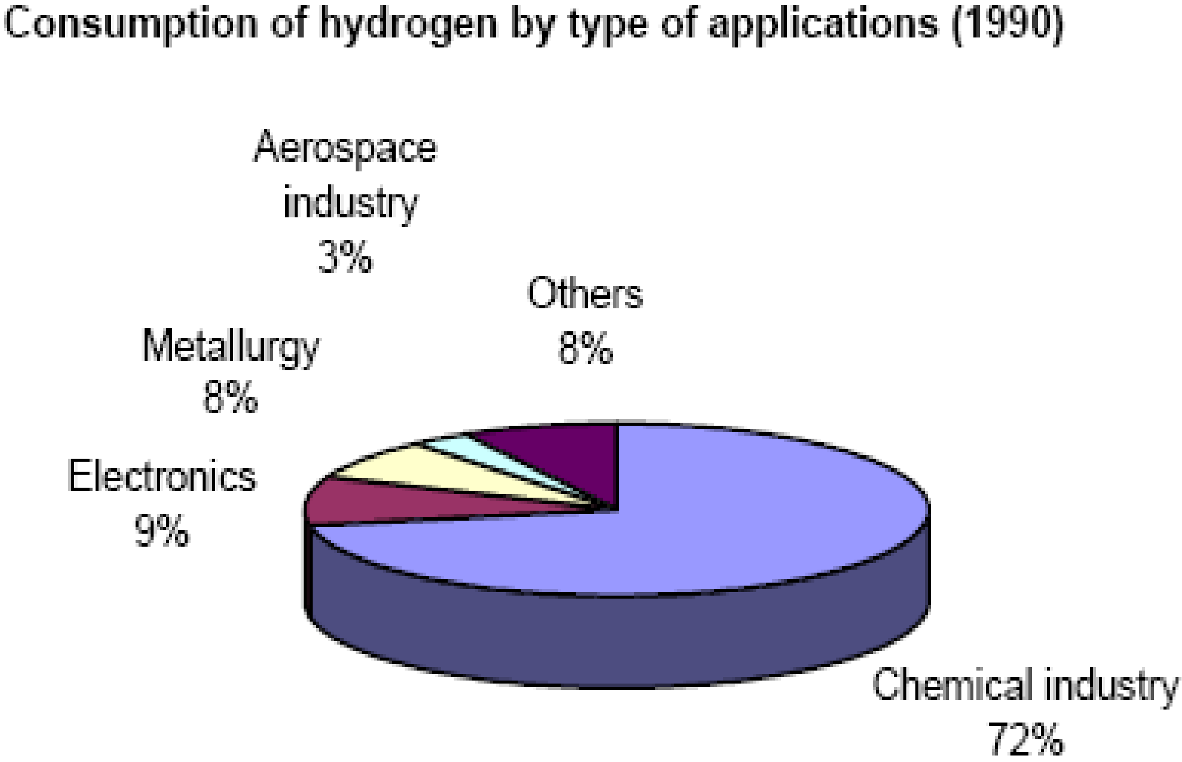


Figure 7 Consumption of Hydrogen by Type of Application (1990)

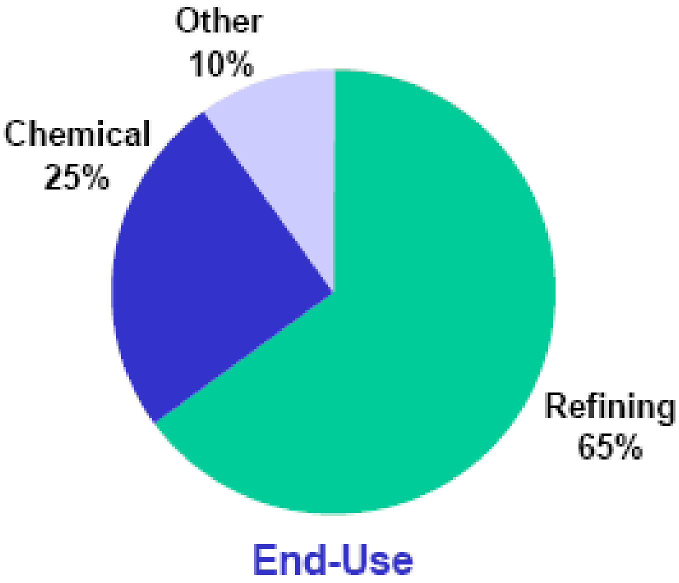


Figure 8 Graph of End-Use of Hydrogen

4.1 Hydrogen Prices

Assuming a 40-year lifetime with zero recovery value, the H_2-MHR could produce hydrogen for about \$1.30/kg. The cost of producing hydrogen from natural gas by steam reformation of methane depends strongly on the cost of the natural gas, which is used for both the feedstock and the energy source. At the current natural gas cost of \$3.50/MBtu, steam reformation can produce hydrogen for about \$1.00/kg. However, if carbon capture and sequestration were required, the estimated cost of \$100/ton of CO_2 would add about 20¢/kg of H_2 to the cost of hydrogen from methane. If the H_2-MHR were able to sell the oxygen produced at the current price of about 5.3¢/kg, it would reduce the cost of nuclear hydrogen production by about 40¢/kg of H_2. This would mean that nuclear production of hydrogen using the Modular Helium reactor coupled to the sulfur-iodine thermochemical water-splitting cycle would be competitive with hydrogen produced from fossil fuels even at today's low prices for natural gas. As the price of natural gas rises with increasing demand and decreasing reserves, nuclear production of hydrogen would become still more cost effective. This could result in a large demand for nuclear power plants to produce the hydrogen.

Chapter 5: Literature Proposed Water Splitting Cycles

5.1 The Sulphur-Iodine Cycle[9]

A paper, written by Brown, Funk and Showalter gathered 25 known cycles and ranked them through a simple set of physical attributes[10]. We took a closer look at five of the more promising cycles:

The Sulfur-Iodine cycle consists of three main reactions, an exothermic prime reaction at 120°C:

$$SO_2 + 2H_2O + I_2 \rightarrow H_2SO_4 + 2HI \quad (1)$$

A sulfuric acid concentration and decomposition being highly endothermic at 800°C:

$$H_2SO_4 \rightarrow \tfrac{1}{2}O_{2(g)} + SO_2 + H_2O \quad (2)$$

Equation (2) is the sulfuric acid decomposition step. This is an endothermic 2-stage reaction:

$$H_2SO_4 \rightarrow H_2O + SO_3 \quad (3)$$

$$2SO_3 \rightarrow 2SO_2 + O_2 \quad (4)$$

The first stage, as seen in equation (4), occurs at a temperature of 400-500°C, whereas the second stage, given by equation (5), occurs at 800°C in the presence of a solid catalyst. And an endothermic Hydrogen-Iodine concentration and decomposition at 450°C

$$2HI \rightarrow H_2 + I_2 \quad (5)$$

Equation (3) is the hydriodic acid decomposition reaction. This is a slightly endothermic reaction and can be conducted in the liquid or gas phase. Figure 1 shows a flowsheet of the SI process. The only input is water and the only products are hydrogen and oxygen. The main problems with this cycle are the difficulty of separating sulfuric acid and hydrogen iodide. This can be remedied by using excess liquid iodine and liquid-liquid extraction. The reaction cluster above shows a continuous process where all chemicals are recycled and no effluent is produced.

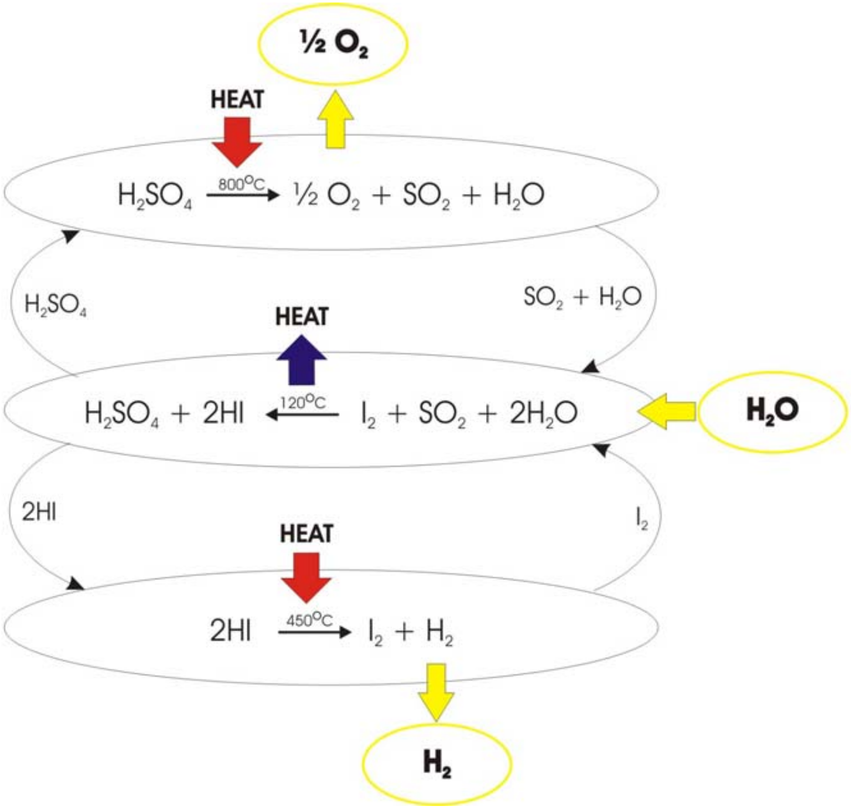


Figure 9 Sulfur-Iodine Cycle

A helium gas cooled reactor was chosen, through different research institutes, as most suitable for coupling to the cycle. It has a high temperature potential and is sufficiently developed for nuclear hydrogen production to be possible with essentially no further development. An intermediate helium loop between the reactor coolant loop and the hydrogen production system is used to ensure that any leakage from the reactor will not contaminate the hydrogen. Using an assumed peak process temperature of 827^{o}C (i.e. a reactor temperature of 850^{o}C) the process efficiency was estimated to be 42%. If the maximum process temperature and reactor temperature are increased to 900°C and 950°C respectively, an efficiency of 52% can be achieved.

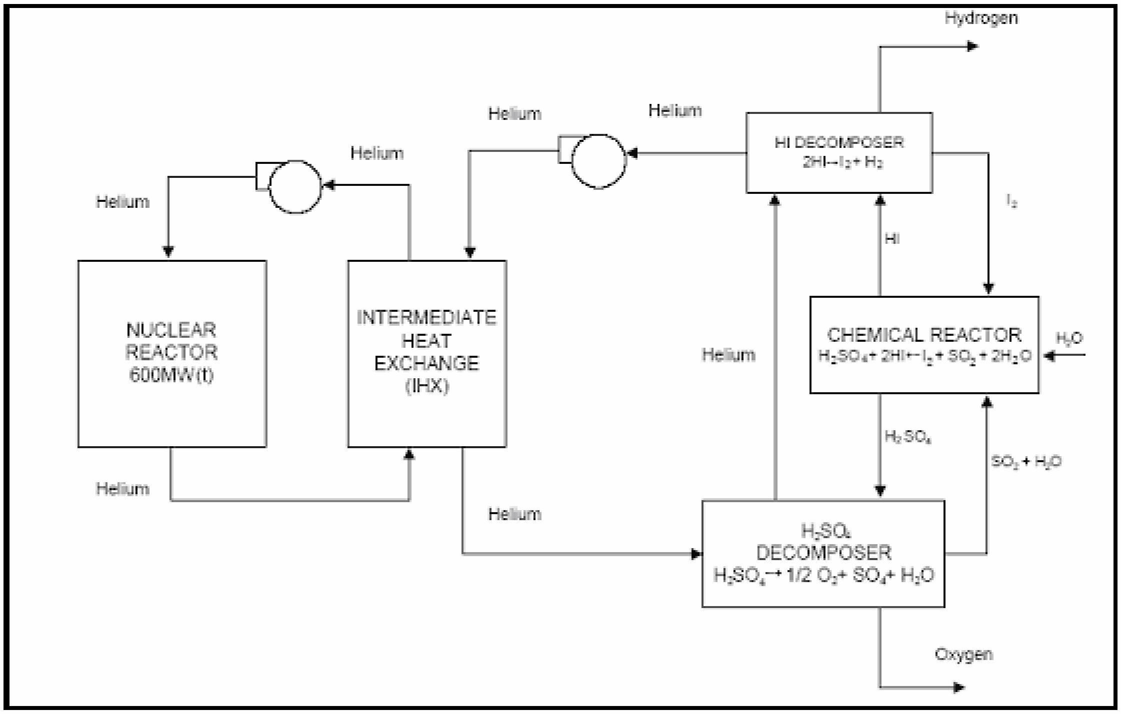


Figure 10 Concept of Modular Helium Reactor with a Sulphur-Iodine Hydrogen Production Plant[11]

5.2 The UT-3 Cycle

The UT-3 cycle was invented at the University of Tokyo and the early development was done there. The Japan Atomic Energy Research Institute (JAERI) selected the so-called Adiabatic UT-3 process for further development. The efficiency of hydrogen generation, for a stand-alone plant, is predicted to be 36% to 40%, depending upon the efficiency of the membrane separation processes. Overall efficiencies can be achieved from 45% to 49%, if a plant co-generates both hydrogen and electricity. It is not clear from published reports if these numbers are based on steady-state operation or if the additional inefficiencies associated with the transient operation were studied. The inefficiencies with transient operation occur when the flow paths are switched.[12]

As with the sulphur-iodine, the reactions involved in the UT-3 cycle vary from a low temperature exothermic reaction to a very high temperature endothermic reaction requiring temperatures up to 760°C.

$$Br_{2(g)} + CaO \rightarrow CaBr_2 + \tfrac{1}{2}O_{2(g)} \qquad (672^\circ\mathrm{C})$$
$$3FeBr_2 + 4H_2O \rightarrow Fe_3O_4 + 6HBr + H_{2(g)} \qquad (560^\circ\mathrm{C})$$
$$CaBr_2 + H_2O \rightarrow CaO + 2HBr \qquad (760^\circ\mathrm{C})$$
$$Fe_3O_4 + 8HBr \rightarrow Br_2 + 3FeBr_2 + 4H_2O \qquad (210^\circ\mathrm{C})$$

This reaction cluster shows a process where all chemicals are recycled and no effluent is produced. This process contains the most understood chemistry of the cycles researched, the reactions are straightforward and simple to achieve, allowing them to go to completion with an efficient membrane separation process. Brown, Funk, and Showalter estimate the efficiency of this cycle to be 36-40%. If used with co-generation of electricity the efficiency can be increased in excess of 60%[13]. The UT-3 process is complicated by having reactions between solids and gases. This requires the use of moving bed reactors, where pairs of Fe_3O_4 / $FeBr_2$ and $CaBr_2$ / CaO beds are switched.

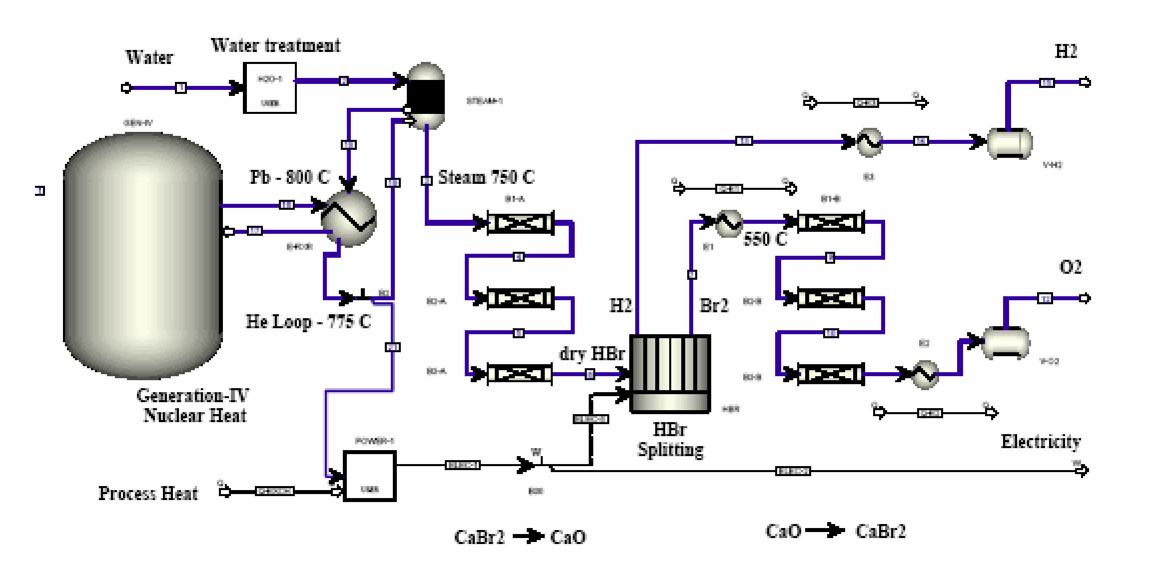


Figure 11 The UT-3 Process Flow Diagram[14]

5.3 The Modified UT-3 Cycle

The modified UT-3 process uses the same principles as the UT-3 cycle, without the iron catalyst, which makes the temperature required to achieve the same conversion 10% higher. The chemical reactions in the modified Ca-Br cycle are given below.

Water splitting with HBr formation (1000 K)

$CaBr_2 + H_2O \rightarrow CaO + 2HBr; \Delta GT = + 2.185$ eV/molecule

Oxygen formation (823 K)

$CaO + Br_2 \rightarrow CaBr_2 + 0.5\ O_2$, $\Delta GT = -0.806$ eV/molecule

Hydrogen production and Bromine regeneration (338 K)

Non-thermal plasma is used; this is low temperature stage with easy separation

$2HBr + \text{plasma} \leftrightarrow H2 + Br_2$, $\Delta GT = + 1.186$ eV/molecule (50% conversion)[15]

Having one less reaction in the cluster reduces the number of separations. This combined with reducing the number of reactors needed allows for less capital investment.

5.4 The Westinghouse Cycle

The Westinghouse sulfur process uses sulfuric acid at high temperatures to create sulfur dioxide and water, which is used in an electrolytic reaction to create hydrogen gas.

$H_2SO_4 \to SO_2 + H_2O + 5O_2$ (800°C)

$2H_2O + SO_2 \to H_2 + H_2SO_4$ (100°C)

The main concern with the sulfur process is the corrosive nature of sulfuric acid and the difficulty in maintaining equipment at a reasonable level. In addition, the use of sulfur dioxide can be a major health risk if any leak is achieved.

Chapter 6: Thermodynamic Analysis

6.0 Heat Cascade Efficiency

The efficiency of a cycle (ε) is defined as the theoretical amount of heat needed to split the water at room temperature (the heat of reaction of the direct splitting reaction, that is the opposite of the heat of formation of water) divided by the amount of heat energy put into the cycle (HU) per mole of water split.

$$\varepsilon = {\Delta H_{RXN}}\big/{HU}$$

The heat requirement for the cycle is given by the hot utility. This is determined using Pinch Analysis, one of the tools of Heat integration.

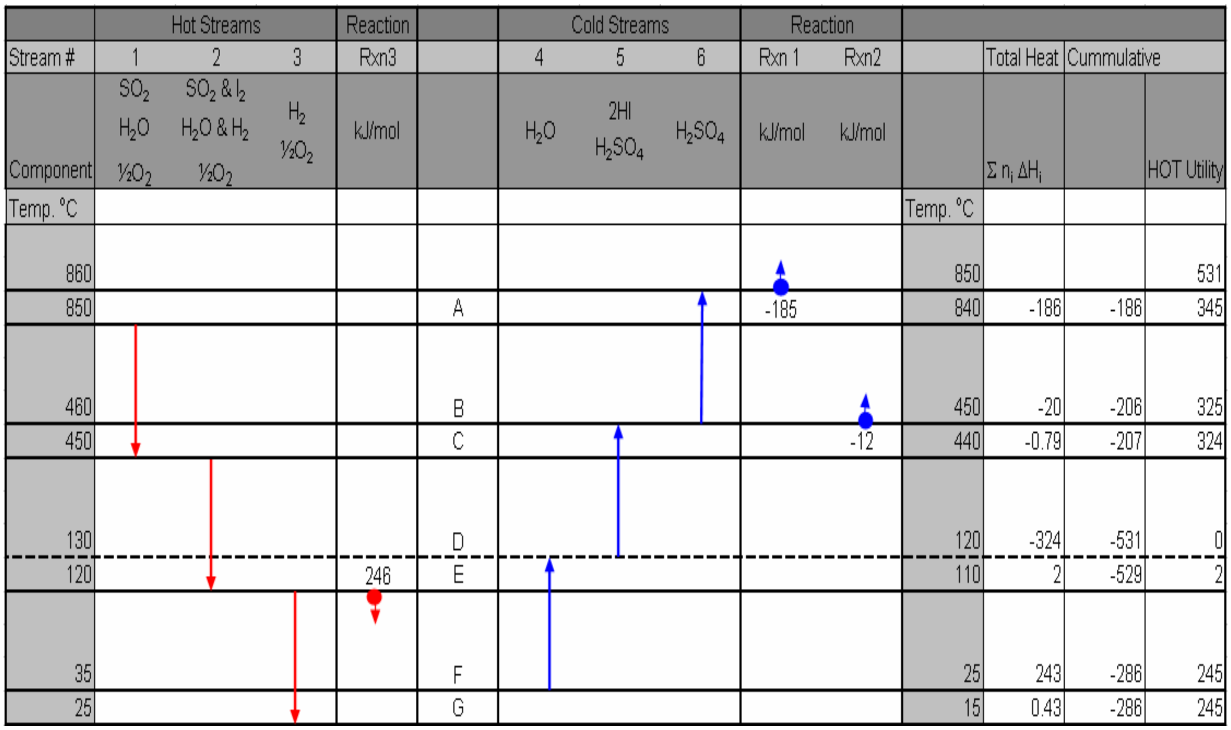
6.1 Heat Cascade Using a Pinch Analysis

This method only determines the energy requirements of the process resulting from heating and cooling chemical species (including phase changes) and from the enthalpy changes of the reactions. This method also includes a 10^{o}C approach temperature between streams. A continuously flowing stream cannot heat another continuously flowing stream all of the way up to the same temperature, it requires an infinite heat transfer surface area, a temperature gradient is required to cause the heat to flow.

The heat cascade analysis begins with a simplified diagram of the cycle. This diagram shows the temperatures at which the reactions occurred and the movement of the chemical species between them. To illustrate this, consider the Sulfur-Iodine cycle. Although, this diagram shows several species lumped together in a “stream” this is not necessarily a real stream in the process. The purpose of these streams is only to show where the chemical species go and what thermodynamic process they must incur along the way. It begins with heating 1 mole of water from 25^{o}C to 115^{o}C. The next interval is also just one mole of water, this time it is heated from 115^{o}C to 125^{o}C.

This small interval is needed because it is necessary for the cooling stream to be always 10^{o}C higher than the heating stream. This way the cooling stream will be able to give heat to the heating stream over its entire range. This is known as pinch analysis and applies to all temperature intervals throughout the cycle.

The mathematics of a pinch point analysis is demonstrated in a temperature interval diagram (Figure 12). From this diagram, it can be seen that the total heat for a temperature interval (zone) is the sum of the enthalpy change of the species multiplied with their molar amounts. The heats of reactions that were included in the heat cascade were calculated in accordance to the 10^{o}C approach temperature. Endothermic reactions receive their heat from cooling streams and exothermic reactions give heat to heating streams. Once these energies are calculated, the heat cascade is used to find the hot utility and cold utility requirements. The hot utility is calculated by using a cumulative sum from the high temperature zone to the low temperature zone. After the cumulative sum is found for each zone, the highest cumulative sum is the hot utility requirement. This hot utility requirement is then subtracted from all of the cumulative zone values. The resulting value for the coolest zone is then the cold utility requirement. All of these calculations are demonstrated in Figure 12.



	Hot Streams			Reaction		Cold Streams			Reaction					
Stream #	1	2	3	Rxn3		4	5	6	Rxn 1	Rxn2		Total Heat	Cummulative	
Component	SO_2 H_2O $½O_2$	SO_2 & I_2 H_2O & H_2 $½O_2$	H_2 $½O_2$	kJ/mol		H_2O	2HI H_2SO_4	H_2SO_4	kJ/mol	kJ/mol		$\Sigma n_i \Delta H_i$		HOT Utility
Temp. °C											Temp. °C			
860											850			531
850					A				-185		840	-186	-186	345
460					B						450	-20	-206	325
450					C					-12	440	-0.79	-207	324
130					D						120	-324	-531	0
120				246	E						110	2	-529	2
35					F						25	243	-286	245
25					G						15	0.43	-286	245

Figure 12 Temperature Interval Diagram plus Heat of Reaction

6.2 Free Energy of Reaction

The Gibbs energy for a reaction serves as an indicator to how easily a reaction will occur. If the Gibbs energy is negative then the reaction will have a higher concentration of products than reactants at equilibrium. A positive Gibbs energy does the opposite; there will be a higher concentration of reactant than products. This suggests that a reaction with a positive Gibbs will not have a very high conversion. Although it is desirable to have a negative Gibbs energy, the problem can be overcome by driving the reaction forward using changes in temperatures and pressures.

6.2.1 Equilibrium Constants

The equilibrium constants (K) were found using the following formula

$$K = \exp\left(\frac{-\Delta G_{RXN}}{RT_{RXN}}\right) = \prod y_i^{\nu_i} \phi_i^{\nu_i} P^{\nu} \quad where \quad \nu = \sum \nu_i$$

where y_i is the mole fraction in the reaction mixture, ϕ_i is the fugacity coefficient, and ν_i is the stoicheometric coefficient of species i[16]. The stoicheometric coefficients are positive for products and negative for reactants. If an ideal gas assumption is made then the fugacity coefficients will be equal to unity. Therefore for a reaction containing all gas species such that $aA + bB + cC + \ldots \rightarrow \ldots + xX + yY + zZ$. Assuming ideal gas behavior of the species

$$K = \frac{y_A^a \cdot y_B^b \cdot y_C^c \cdot \ldots}{\ldots \cdot y_X^x \cdot y_Y^y \cdot y_Z^z} \cdot P^{\nu}$$

Using this and molar accounting as the reactants are converted to the products; it is possible to determine the molar composition of the reaction mixture at equilibrium when given an initial reactor feed.

6.2.2 Thermodynamic Analysis of Known Cycles

The appendix provides step-by step calculations of the efficiencies of the cycles, Gibbs energy of the reactions, and equilibrium constants of the reactions. Table 3 summarizes these results.

6.3 Results of Thermodynamic Analysis

Table 3 List of Reaction Cluster for Cycles[17]

Cycle	Name	Temperature	Reaction	Δ G	K	Efficiency
1	US -Chlorine	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	-17.43	6.466	**99.9%**
		200	$2CuCl + 2HCl \rightarrow 2CuCl_2 + H_2(g)$	-5.79	2.462	
		500	$2CuCl_2 \rightarrow 2CuCl + Cl_2(g)$	143.68	1.37534E-16	
2	Hallett Air Products	800	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	-14.02	4.811	**99.7%**
		25	$2HCl \rightarrow Cl_2(g) + H_2(g)$	162.32	3.64892E-29	
3	Westinghouse	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	-68.36	1510	**81.7%**
		77	$SO_2 (g) + 2H_2O(a) \rightarrow H_2SO_4(a) + H_2(g)$	44.23	2.52718E-07	
4	Ispra Mark 4	850	$2Cl_2(g) + 2H_2O(g) \rightarrow 4HCl(g) + O_2(g)$	-17.43	6.466	**77.9%**
		100	$2FeCl_2 + 2HCl + S \rightarrow 2FeCl_3 + H_2S$	189.21	6.178E-10	
		420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	15.94	0.06296	
		800	$H_2S \rightarrow S + H_2(g)$	105.34	1.796E-15	
5	Gaz de France	725	$2K + 2KOH \rightarrow 2K_2O + H_2(g)$	159.47	2.600E-08	**56.2%**
		825	$2K_2O \rightarrow 2K + K_2O_2$	141.86	3.770E-08	
		125	$2K_2O_2 + 2H_2O \rightarrow 4KOH + O_2(g)$	-217.89	3.84112E+28	
6	Julich Center EOS	800	$2Fe_3O_4 + 6FeSO_4 \rightarrow 6Fe_2O_3 + 6SO_2 + O_2(g)$	-91.00	26879	**54.1%**
		700	$3FeO + H_2O \rightarrow Fe_3O_4 + H_2(g)$	19.29	0.09222	
		200	$Fe_2O_3 + SO_2 \rightarrow FeO + FeSO_4$	-18.04	98.03	
7	Sulfur-Iodine	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	-68.36	1510	**53.8%**
		450	$2HI \rightarrow I_2(g) + H_2(g)$	23.59	0.019770129	
		120	$I_2 + SO_2(a) + 2H_2O \rightarrow 2HI(a) + H_2SO_4(a)$	-36.79	77134	
8	Ispra Mark 7B	1000	$2Fe_2O_3 + 6Cl_2(g) \rightarrow 4FeCl_3 + 3O_2(g)$	141.87	1.513E-06	**51.6%**
		420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	48.63	0.001771369	
		650	$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2(g)$	23.90	0.01580	
		350	$4Fe_3O_4 + O_2(g) \rightarrow 6Fe_2O_3$	-39.37	1135	
		400	$4HCl + O_2(g) \rightarrow 2Cl_2(g) + 2H_2O$	-76.64	2657047.645	
9	UT-3 Univ. Tokyo	600	$2Br_2(g) + 2CaO \rightarrow 2CaBr_2 + O_2(g)$	101.89	6.28583E-06	**47.6%**
		600	$3FeBr_2 + 4H_2O \rightarrow Fe_3O_4 + 6HBr + H_2(g)$	-37.95	186.28	
		750	$CaBr_2 + H_2O \rightarrow CaO + 2HBr$	-95.07	461816604	
		300	$Fe_3O_4 + 8HBr \rightarrow Br_2 + 3FeBr_2 + 4H_2O$	122.93	4.42731E-08	
10	Ispra Mark 13	850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	-68.36	1510	**46.6%**
		77	$2HBr(a) \rightarrow Br_2(a) + H_2(g)$	-125.55	5.36365E+18	
		77	$Br_2 (l) + SO_2(g) + 2H_2O(l) \rightarrow 2HBr(g) + H_2SO_4(a)$	169.78	4.71168E-26	
11	Ispra Mark 9	420	$2FeCl_3 \rightarrow Cl_2(g) + 2FeCl_2$	48.63	0.001771	**44.2%**
		150	$3Cl_2(g) + 2Fe_3O_4 + 12HCl \rightarrow 6FeCl_3+6H_2O+O_2(g)$	23.90	0.015799	
		650	$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2(g)$	-19.98	292.2	
12	GA Cycle 23	800	$H_2S(g) \rightarrow S(g) + H_2(g)$	-136.71	2279787.497	**36.0%**
		850	$2H_2SO_4(g) \rightarrow 2SO_2(g) + 2H_2O(g) + O_2(g)$	189.21	6.178E-10	
		700	$3S + 2H_2O(g) \rightarrow 2H_2S(g) + SO_2(g)$	-230.20	2.270E+12	
		25	$3SO_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(a) + S$	-290.18	6.86346E+50	
		25	$S(g) + O_2(g) \rightarrow SO_2(g)$	-300.12	3.78213E+52	
13	Mark 7A	420	$2FeCl_3(l) \rightarrow Cl_2(g) + 2FeCl_2$	47.29	0.01148	**30.2%**
		650	$3FeCl_2 + 4H_2O(g) \rightarrow Fe_3O_4 + 6HCl(g) + H_2(g)$	48.63	0.001771369	
		350	$4Fe_3O_4 + O_2(g) \rightarrow 6Fe_2O_3$	23.90	0.01580	
		1000	$6Cl_2(g) + 2Fe_2O_3 \rightarrow 4FeCl_3(g) + 3O_2(g)$	-76.64	2657047.645	
		120	$Fe_2O_3 + 6HCl(a) \rightarrow 2FeCl_3(a) + 3H_2O(l)$	69.65	5.573E-10	

Chapter 7: Molecular Discovery

7.1 Introduction

Molecular discovery was used in an attempt to supplement the list of water-splitting cycles available for analysis. In the previous sections, all of the water-splitting cycles discussed were found from a search of published articles. Most of these were proposed by chemists who realized the potential of combining some known reactions. Not many scientists, however, have tried an automated, systematic approach to finding more cycles. This is where the method of molecular discovery is useful.

Molecular discovery is the use of a set of algebraic constraints and an objective function to find the optimal solution for the model. The value of the objective function is either maximized or minimized depending on the user specification. An algebraic model solver such as GAMS searches the different combinations of the input data for the combination that both satisfies the constraint equations and optimizes the objective function.

An algebraic model can be used to find a cluster of chemical species that represent a water-splitting cycle. The chemical species in this cluster must satisfy physical, thermodynamic, and chemical constraints. The algebraic model contains statements that represent the true system. An example of this is the constraint that states that the number of one type of atom has to be the same on both sides of the chemical equation. Other constraints ensure that each reaction are less than the user specified maximum Gibbs energy, the total cluster results in the splitting of water into oxygen and hydrogen, and that the stoichiometric coefficients of each species are integer values. There are many more constraints, for the complete list see the appendix.

As discussed before, the heat cascade analysis gives an initial indication of the maximum efficiency of the cycle. Since the heat cascade efficiency is inversely proportional to the hot utility requirement determined from a heat cascade analysis, it would be useful to find new cycles that minimize the hot utility requirement. Of course, these cycles would need further analysis to determine if other inefficiencies such as separations significantly reduce the overall efficiency of the cycle. GAMS can be used to find a cluster of chemical species that make a cycle that minimizes the hot utility requirement yet meets all of the constraints.

7.1.1 Previous Studies

The method of molecular discovery was proposed by Holiastos and Manousiouthakis to find reaction clusters with more favorable Gibbs energies than the direct reaction they replace. Holiastos and Manousiouthakis show that for any reaction that can be replaced by a two-reaction cycle, if the two reactions are feasible at within a range of temperatures, they are also feasible at the boundaries of the temperature range. Holiastos and Manousiouthakis also show that Gibbs energy of a reaction is almost linear as a function of temperature. Therefore, to simplify their model, they used linear estimates of the Gibbs energy of reaction. Their model also contains an objective function that minimizes the number of chemical species in the reaction cluster. Minimizing the number of species in the reaction cluster does not have as much relevance to the operating cost of a cycle as the hot utility requirement.

7.1.2 Modified Model

Constraints were added to the original model that evaluated the hot utility requirements for each reaction cluster. The result of this analysis was used as the value of the objective function. This way GAMS could search for a feasible reaction that minimizes the hot utility requirement. Since the heat cascade required enthalpies of each species, it was necessary to replace the linear Gibbs estimates with the more complicated Shomate equations. The Gibbs energy was calculated in a similar manner as described above, from the enthalpy and entropy of each species as a function of temperature. The entropies and enthalpies were determined from the Shomate equations. In addition, constraints were added that prevented the same chemical species from appearing on both sides of the same chemical equation (non-participant species were eliminated). Finally, constraints were added that prevented both hydrogen and oxygen from being products of the same reaction.

7.1.3 Results

The best result found with this model is shown below along with the data in Table 4 Molecular Discovery Results. The chemical species included in this model are shown in Table 4. Other user-defined parameters are shown in Table 6.

$$\tfrac{1}{2}C_3H_6O \rightarrow \tfrac{1}{2}C_2H_2 + H_2 + \tfrac{1}{2}CO \qquad (1400K)$$

$$\tfrac{1}{2}C_2H_2 + H_2O + \tfrac{1}{2}CO \rightarrow \tfrac{1}{2}O_2 + \tfrac{1}{2}C_3H_6O \qquad (400K)$$

Gibbs Energy of First Reaction	9.33 kJ/mol
Gibbs Energy of Second Reaction	18.9 kJ/mol
Heat of First Reaction	416 kJ/mol
Heat of Second Reaction	14.8 kJ/mol
Hot Utility Requirement	414 kJ/mol H_2
Cascade Efficiency	70.0

Table 4 Molecular Discovery Results

GAMS#	Species	GAMS#	Species
i1	Acetylene	i25	Potassium Peroxide
i2	1,1 Dichloroethane	i26	Copper(I) Oxide
i3	1,1,1-Trichloroethane	i27	Copper(II) Oxide
i4	Chloroethene	i28	Copper(II) Chloride
i5	Chloroethane	i29	Bromine Chloride
i6	Ethanol	i30	Dichloroethyne
i7	Carbon Monoxide	i31	Ketene
i8	Carbon Dioxide	i32	Bromoethene
i9	Chlorine	i33	Ethene
i10	Tetrachloroethene	i34	Bromoethane
i11	Hydrogen	i35	Ethane
i12	Water	i36	Ethylamine
i13	Oxygen	i37	Acetone
i14	Bromine	i38	Propane
i15	Hydrogen Bromide	i39	Formaldehyde
i16	Hydrogen Chloride	i40	Bromomethane
i17	Hydrogen Iodide	i41	Chloromethane
i18	Hydrogen Sulfide	i42	Methylamine
i19	Sulfur Dioxide	i43	Nitromethane
i20	Sulfuric Acid	i44	Methylnitrate
i21	Calcium Oxide	i45	Methanol
i22	Iron(II) Oxide	i46	Methane
i23	Iron(II) Sulfate	i47	Hydrogen Peroxide
i24	Iron(III) Oxide		

Table 5 Chemical Species Included in Model

Thermodynamic Feasibility Tuning Factor	-0.0002419
High Temperature	400 K
Low Temperature	1400 K
Maximum Number of a Species per side of Reaction	4
Minimum number of a Species per side of Reaction	1
Maximum Total Number of Species per side of Reaction	4
Minimum Total Number of Species per side of Reaction	1

Table 6 Model Parameters

7.1.4 Limitations of Model

The modified model calculates the heat cascade based on the upper and lower reaction temperatures. Because of this, the new model does not necessarily find the feasible reaction set in the temperature range with the lowest hot utility requirement. Instead, it finds a feasible reaction set with the lowest hot utility for reactions fixed at the specified temperatures. Because of this, a truly exhaustive search of the lowest hot utility would require systematically setting the model parameters for the reaction temperatures to try all possible combinations.

The Shomate equation parameters have a specified temperature range for which they can be used. Breaks in the range are seen especially when a species undergoes a phase change. The modified model is not able to choose the correct set of Shomate parameters that match the temperature. Therefore, it is necessary to pre-select the species so that they have only one set of parameters for a specified temperature range. This limitation eliminates the use of species that undergo phase changes over the specified temperature range. The only exception to this is water. The values for liquid water are entered in the model as constants.

Because the model only bases the feasibility of a reaction on Gibbs energy of reaction, it lacks the ability to discern if a reaction will really happen. In other words, a catalyst might be needed for the reaction to occur at a practical rate.

Chapter 8: Conclusions and Results

8.0 Summary of Results

All of the cycles that were analyzed had at least one reaction with a positive Gibbs energy. This means that these reactions will not have a very high conversion. Possible solutions to this problem utilize Le Chatelier's principal, which states that when a system at equilibrium is disturbed, the equilibrium conditions shift to counteract the disturbance. Therefore, the usage of a large excess of the recycled reactant in the reaction raises the concentration of that species as compared to the others. This forces the formation of more products to maintain the same equilibrium constant. Other solutions would be to remove the products as they are formed or change the pressure of the reaction vessel.

The Hallett Air Products cycle was chosen for deeper investigation because of its very high efficiency, ease of moving the all-gas chemical species, and the overall simplicity of the cycle. Because this cycle only has two reactions in it, it will not require as many mixture separations. The low temperature reaction has a very small equilibrium constant, but it might be possible to force the reaction to proceed by either removing the hydrogen with a permeable membrane or by adding excess amounts of HCl. Increasing the amount of HCl is still a problem however because this makes removing the products from the reactor effluent more difficult. It is possible that this difficulty could take so much energy that it makes the thermodynamic efficiency unimportant. Preliminary research shows no evidence of an effective membrane. In addition, an unrealistic amount of HCl is required to make the reaction proceed to make the necessary amount of H_2.

Hallett Air Product Cycle with Transportation & Storage

The Investor's Rate of Return (IRR) for this Project is:	**10.28%**
The Net Present Value (NPV) at 10% for this Project is:	**$ 30,605,100.00**

ROI Analysis (Third Production Year)

Annual Sales:	$390,270,200
Annual Costs:	-367,963,000.00
Depreciation:	-78,607,200.00
Income Tax:	$20,831,000
Net Earnings:	$43,138,200
Total Capital Investment:	$1,107,337,800
ROI:	**3.90%**

Table 7 Profitability of Hallett Air Product Investment

Sulphur Iodine Cycle with Transportation & Storage

The Investor's Rate of Return (IRR) for this Project is:	**8.26%**
The Net Present Value (NPV) at 10% for this Project is:	**-247,152,500.00**

ROI Analysis (Third Production Year)

Annual Sales:	390,270,200.00
Annual Costs:	-388,301,600.00
Depreciation:	-107,578,200.00
Income Tax:	39,075,600.00
Net Earnings:	41,044,200.00
Total Capital Investment:	1,512,901,900.00
ROI:	**2.70%**

Table 8 Profitability of Sulfur-Iodine Investment

The analysis of the thermodynamic efficiency is not complete until separations processes are considered. Although the Hallett Air Products cycle shows a high efficiency with the heat cascade analysis, most of the energy required to operate this analysis will be needed for separation processes.

Because of the value of energy and raw materials, the ideal cycle would be the one with the best heat cascade efficiency, the most efficient separation process, and lowest total capital investment. In addition, it is important to avoid difficulties with phases of the chemicals. Reactions with two solid reactants are almost impossible to do because the mobility of the molecules is limited. Separations of solid mixtures are difficult if not impossible.

8.1 Varying Reaction Temperatures

The set up of the excel spreadsheet allows for the temperatures of the reactions to be varied and the resulting cascade to be automatically calculated for the efficiency. The Gibbs energies and equilibrium constants are also automatically updated for a temperature change. When the temperatures of the reactions in the Hallett Air Products cycle were changed to 1000^{o}C and 970^{o}C, the efficiency remained essentially unchanged, but the equilibrium constant increased to 2.9×10^{-4}. Assuming a feed mixture to the low temperature reactor consisting of 99% HCl and 1% Cl_2, requires a mass flow rate of 44,000 kg of HCl through the reactor to get the desired production rate of 1000 kg of H_2 per day.

8.2 Final Comments and Ideas

There are two credible energy futures: Electricity is the largest long-distance energy carrier, or hydrogen is the largest long-distance energy carrier. At this time, it is hard to predict which direction the world will take or when it will make that choice. The decision depends on both the success of scientists and engineers and institutional factors. If the nuclear industry wants to assure itself a major role in any future, however, it must be prepared for either alternative. If the nuclear industry chooses to address global warming and energy independence, methods to make hydrogen economical using nuclear energy must be created. Development of economic hydrogen production methods using nuclear power is a major technical challenge that should not be underestimated. Such a path forward provides a powerful vision for the future, however, with nuclear energy being used to address the major issues of industrial societies.[18]

8.2.1 Future Work for Molecular Discovery

- Automatic selection of applicable Shomate constants for a chemical species according to temperature
    - This will extend the temperature range that can be searched (allows for phase changes of species)
- Give list of top results
- Explore possibility of three reaction sets
- Exhaustive search of temperature range settings
    - Using a control loop

8.3 Hydrogen Fuel Cell versus Electric

Our team was asked to investigate the market and possibility of either producing hydrogen for Hydrogen Fuel Cell cars or generating electricity to meet the increasing demand and to supply enough for the demand of electric cars. According to the latest data from the Energy Information Administration, 428 gigawatts of new generating capacity will be needed by 2025 to meet the growing demand for electricity. This is equivalent to 1,427 new power plants (300 megawatts each). Our team has found that it would not be economically feasible to produce hydrogen. It was investigated further that producing electricity for our new market of electric cars is more profitable.

8.3.1 Recent History of Electric Vehicles (EV)

Much work has been done to promote the EV during the 90's, especially in California. During this time, the predominant battery was lead-acid. Of all of the batteries considered for EV uses now, the lead-acid has the lowest specific energy (energy per weight of battery). The low specific energy caused the test vehicles that used them to have very limited ranges of about 50 miles per charge. In the late 90's nickel metal hydride batteries were being developed. This type of battery was incorporated into the test vehicles and allowed them to have a greater range of about 100 miles per charge. In either case, people are concerned that they would be stuck with a car that they could not rely on to get them to their usual destinations without the hassle of waiting for a recharge. Many have proposed ways to decrease the time it takes to charge the batteries in the cars, but even the quickest systems take nearly ten minutes. Even more, it is not possible to do a full recharge in this period. Unusually, many people have put forth a lot of effort in these lines yet have not proposed the seemingly obvious solution. Why are people not making standardized systems so that a fully recharged battery can be swapped for the discharged battery? Would this be economically feasible, and how would it be done?

8.3.2 Possible Solution

The proposal that will be looked at is establishing recharging stations that have batteries on hand that are being recharged so that a person can swap a discharged battery for a recharged one. These batteries would have to be sold with some sort of guarantee that they will produce to some minimum performance. This guarantee should be simple to uphold if the station maintains the battery correctly.

8.3.3 Comparative Energy Costs

Based on economic analysis, the electricity (or energy costs) is much less than those needed for water splitting (222 vs. 1000 MWe for 1 million people). In addition, the thermal energy required per mile of driving for the electric vehicle is **1,524 kJ/mile** compared to the hydrogen fuel cell car, which is **6,500 kJ/mile**. This estimate includes all of the costs from the power plant to the vehicle.

8.3.4 Market Start-up

There is little information on how much a HFC car will cost, but initial indications are that it will be two to three times more than a standard internal combustion vehicle. On the other hand, EVs have many of the same components as Hybrids, so they are expected to cost about the same. Actually, there is potential for EVs to be even cheaper because they are less complicated than Hybrids. The cost of the vehicle is important because the consumer is more likely to purchase the vehicle if it is affordable.

In addition to this, the scalability is much more flexible for EVs. The possibility of a city-by-city switch over is made easier because the infrastructure for getting the necessary electricity is mostly in place. There will be a need to strengthen the power grid. This can be done if the power companies charge a premium for this type of service. The price requirement for added infrastructure should be much less to the infrastructure price needed for the manufacture and distribution of hydrogen (EV will require less energy, also aluminum power lines should be cheaper than large, thick, stainless steel pipelines). EV station profitability should not be limited by how close it is to a nuclear power plant. Even more flexibility is added by the fact that the thermochemical water-splitting cycles can only work when attached to a nuclear plant. It is recognize that using electric vehicles would move the source of pollution to the power plants. However, regulating and maintaining power plants are easier than individual vehicles.

Chapter 9: Previous Studies

9.0 Summary[19]

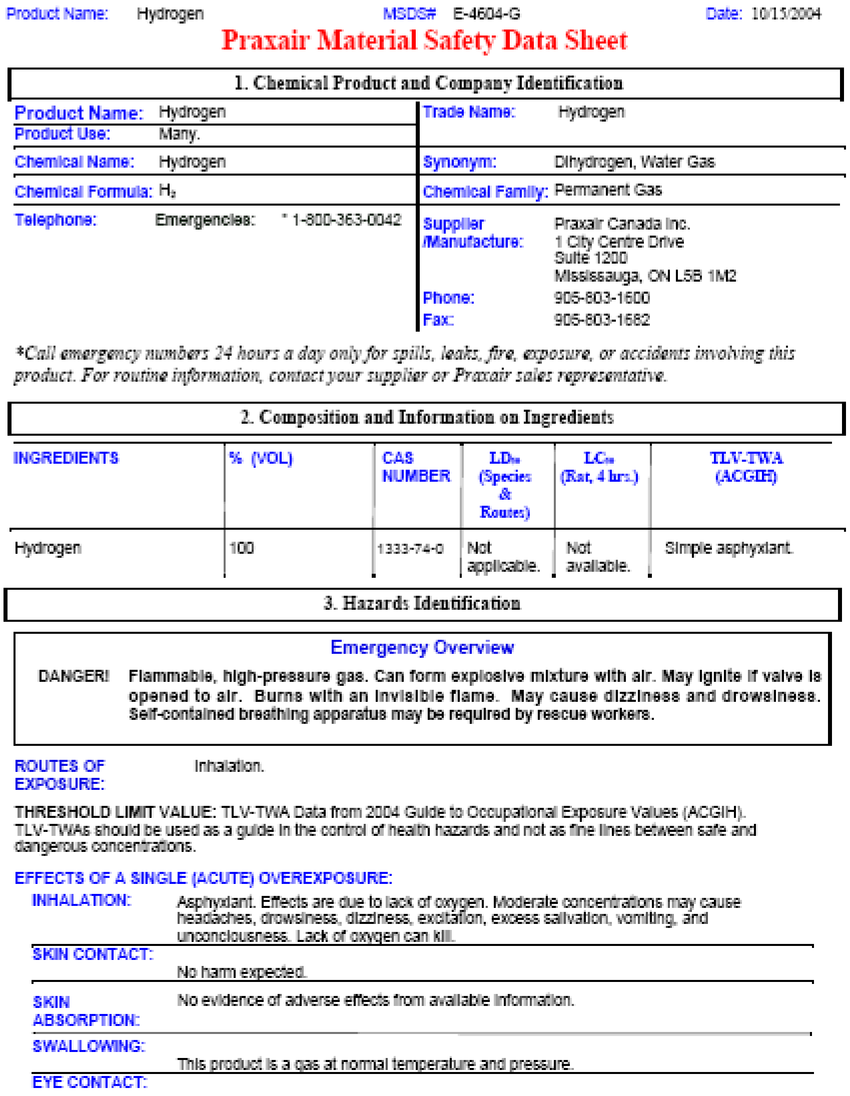
The first major program was at the European Community Joint Research Center (ISPRA), beginning in the late 1960s and continuing through 1983. The goal of this work was to identify thermochemical cycles to couple to the high temperature, gas-cooled reactor. The three-phase program investigated 24 cycles. In phase I, thermochemical cycles were developed based on the chemistries of mercury, manganese, and vanadium. In phase II, nine cycles based on iron chloride chemistry were investigated. The iron chloride cycles were abandoned because of the difficulties with the thermal decomposition of ferric chloride. Later, the Gas Research Institute identified a proprietary procedure that may have resolved these issues. Phase III focused on multiple sulfur-based cycles with a laboratory demonstration of the sulfur-bromine hybrid process. Associated with these laboratory efforts were parallel activities involving corrosion testing, design of larger-scale equipment, and development of industrial flowsheets. The duration (1.5 yrs) of the sulfur-bromine hybrid laboratory test is the most extensive demonstration of any thermochemical cycle to date. In the United States, the Gas Research Institute (now known as the Gas Technology Institute) funded a long-term program that systematically examined thermochemical cycles. Over the nine-year program, 200 distinct thermochemical cycles were examined, about 125 cycles were considered feasible based on thermodynamic considerations, 80 of the most promising cycles were tested in the laboratory, 15 of these cycles were found to be operable using batch techniques with reagent-grade chemicals, and eight cycles were operated successfully with recycled materials to achieve proof-of-principle. This work is the single most comprehensive source of information on thermochemical cycles. The heat source for these cycles was to be either a nuclear reactor or a solar system, and cycles covering a wide range of temperatures were considered. Several conclusions were drawn from the Gas Research Institute work. The most important conclusion was that experimental verification is required to determine if a thermochemical cycle is viable. Analyses alone are not sufficient. Most proposed cycles were eliminated in the laboratory because the chemical reactions were too slow, unwanted chemical reaction products were produced, or no efficient methods were found to separate chemical reaction products. New developments in catalysts or separations techniques could make some of these processes viable. The second conclusion was that there are very large differences between theoretical efficiencies and efficiencies based on initial process flow sheets; thus, processes that have high theoretical efficiencies may not work in practice. The conclusion of this work was that relatively few of the cycles investigated were promising for further development. The three that were most highly ranked were hybrid sulfur, sulfur iodine, and hybrid copper sulfate.

The largest single-process development effort was conducted by Westinghouse Corporation to develop the hybrid sulfur process. This effort progressed through a laboratory demonstration with the final product being a conceptual design report for a pilot plant. Two conclusions are derived from this work: first, the hybrid sulfur process with 1970s technologies could be made to work and second, there were many options to improve efficiency ─ given sufficient R&D resources. Process efficiencies above 40% were calculated for these hybrid sulfur experiments; however, potential improvements were also identified that could significantly increase efficiency. With the decrease in energy prices in the late 1970s, all of these efforts (except for a small effort in Japan) were abandoned. More recently (1999), based on the renewed interest in hydrogen production, General Atomics, Sandia National Laboratories, and the University of Kentucky jointly conducted a literature evaluation of thermochemical processes. The Nuclear Energy Research Initiative (NERI) study reviewed available information for 115 cycles, which were ranked by complexity (reactions, separations, elements, corrosiveness), development maturity (demonstration level, publications), and performance (efficiency, cost). The four leading processes were hybrid sulfur, sulfur-bromide hybrid, UT-3 (calcium bromine), and sulfur-iodine. The "new" process was the UT-3 process developed by the University of Tokyo since the 1970s. The work on this new cycle was initiated to provide a lower-temperature process that would be compatible with lower-temperature heat sources.

The general conclusion of these studies is there are currently a small number of processes that can be considered as candidates for large-scale development. Given the scope of research in the 1970s, it is judged relatively unlikely that a significant number of new cycles with more promising chemistry will be identified in the near term. It is recognized that new technologies (catalysts and separations techniques) may make previously unattractive thermochemical cycles viable. Although many cycles should be reevaluated in light of these new technologies, they cannot yet be considered candidates for near-term development.

Chapter 10: Appendix

10.0 Hydrogen MSDS



Product Name: Hydrogen MSDS# E-4604-G Date: 10/15/2004

Praxair Material Safety Data Sheet

1. Chemical Product and Company Identification

Product Name:	Hydrogen	**Trade Name:**	Hydrogen
Product Use:	Many.		
Chemical Name:	Hydrogen	**Synonym:**	Dihydrogen, Water Gas
Chemical Formula:	H_2	**Chemical Family:**	Permanent Gas
Telephone:	Emergencies: * 1-800-363-0042	**Supplier /Manufacture:**	Praxair Canada Inc. 1 City Centre Drive Suite 1200 Mississauga, ON L5B 1M2
		Phone:	905-803-1600
		Fax:	905-803-1682

**Call emergency numbers 24 hours a day only for spills, leaks, fire, exposure, or accidents involving this product. For routine information, contact your supplier or Praxair sales representative.*

2. Composition and Information on Ingredients

INGREDIENTS	% (VOL)	CAS NUMBER	LD_{50} (Species & Routes)	LC_{50} (Rat, 4 hrs.)	TLV-TWA (ACGIH)
Hydrogen	100	1333-74-0	Not applicable.	Not available.	Simple asphyxiant.

3. Hazards Identification

Emergency Overview

DANGER! **Flammable, high-pressure gas. Can form explosive mixture with air. May ignite if valve is opened to air. Burns with an invisible flame. May cause dizziness and drowsiness. Self-contained breathing apparatus may be required by rescue workers.**

ROUTES OF EXPOSURE: Inhalation.

THRESHOLD LIMIT VALUE: TLV-TWA Data from 2004 Guide to Occupational Exposure Values (ACGIH). TLV-TWAs should be used as a guide in the control of health hazards and not as fine lines between safe and dangerous concentrations.

EFFECTS OF A SINGLE (ACUTE) OVEREXPOSURE:

INHALATION:	Asphyxiant. Effects are due to lack of oxygen. Moderate concentrations may cause headaches, drowsiness, dizziness, excitation, excess salivation, vomiting, and unconciousness. Lack of oxygen can kill.
SKIN CONTACT:	No harm expected.
SKIN ABSORPTION:	No evidence of adverse effects from available information.
SWALLOWING:	This product is a gas at normal temperature and pressure.
EYE CONTACT:	

No harm expected.

EFFECTS OF REPEATED (CHRONIC) OVEREXPOSURE:
Not available.

OTHER EFFECTS OF OVEREXPOSURE:
Asphyxiant. Lack of oxygen can kill.

MEDICAL CONDITIONS AGGRAVATED BY OVEREXPOSURE:
Repeated or prolonged exposure is not known to aggravate medical condition.

SIGNIFICANT LABORATORY DATA WITH POSSIBLE RELEVANCE TO HUMAN HEALTH HAZARD EVALUATION:
None currently known.

CARCINOGENICITY:
Not listed as carcinogen by OSHA, NTP or IARC.

4. First Aid Measures

INHALATION:

Remove to fresh air. If not breathing, give artifical respiration. If breathing is difficult, qualified personnel may give oxygen. Call a physician.

SKIN CONTACT:

Wash with soap and water.

SWALLOWING:

This product is a gas at normal temperature and pressure.

EYE CONTACT:

Flush with water.

NOTES TO PHYSICIAN:

There is no specific antidote. Treatment of over-exposure should be directed at the control of symptoms and the clinical condition.

5. Fire Fighting Measures

FLAMMABLE :	Yes.	**IF YES, UNDER WHAT CONDITIONS?**	See Unusual Fire and Explosion Hazards.
FLASH POINT (test method)	Not applicable.	**AUTOIGNITION TEMPERATURE**	520°C (968°F)
FLAMMABLE LIMITS IN AIR, % by volume:	**LOWER:** 4	**UPPER:**	75

EXTINGUISHING MEDIA:

CO2, dry chemical, water spray or fog.

SPECIAL FIRE FIGHTING PROCEDURES:

DANGER! Evacuate all personnel from danger area. Immediately cool cylinders with water spray from maximum distance taking care not to extinguish flames. Remove ignition source if without risk. If flames are accidentally extinguished. explosive re-ignition may occur; therefore, appropriate measures should be taken; e.g., total evacuation. Reapproach with extreme caution. Use self-contained breathing apparatus. Stop flow of gas if without risk while continuing cooling water spray. Remove all containers from area if without risk. Allow fire to burn out.

UNUSUAL FIRE AND EXPLOSION HAZARD:

Flammable gas. Flame is nearly invisible. Escaping gas may ignite spontaneously. Hydrogen has a low ignition energy. Fireball forms if gas cloud ignites immediately after release. Forms explosive mixtures with air and oxidizing agents. Heat of fire can build pressure in cylinder and cause it to rupture. No part of a cylinder should be subjected to a temperature higher than 52 C. Cylinders are equipped with a pressure-relief device. (Exceptions may exist where authorized by TDG regulations.) If venting or leaking gas catches fire, do not extinguish flames. Flammable gas may spread from leak, creating an explosive re-ignition hazard. Vapors can be ignited by pilot lights, other flames, smoking, sparks, heaters, electrical equipment, static discharge, or other ignition sources at locations distant from product handling point. Explosive atmospheres may linger. Before entering area, especially confined areas, check atmosphere with an appropriate device.

HAZARDOUS COMBUSTION PRODUCTS:

None currently known.

SENSITIVITY TO IMPACT:

Avoid impact against container.

SENSITIVITY TO STATIC DISCHARGE:

Possible, ground all equipment.

6. Accidental Release Measures

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED:

DANGER! **Flammable, high-pressure gas.** Forms explosive mixtures with air. Immediately evacaute all personnel from danger area. Use self-contained breathing apparatus where needed. Remove all sources of ignition if without risk. Reduce gas with fog or fine water spray. Shut off flow if without risk. Ventilate area or move cylinder to a well-ventilated area. Flammable gas may spread from leak. Before entering area, especially confined areas, check atmosphere with an appropriate device.

WASTE DISPOSAL METHOD:

Prevent waste from contaminating the surrounding environment. Keep personnel away. Discard any product, residue, disposable container, or liner in an environmentally acceptable manner, in full compliance with federal, provincial, and local regulations. If necessary, call your local supplier for assistance.

7. Handling and Storage

PRECAUTIONS TO BE TAKEN IN STORAGE:

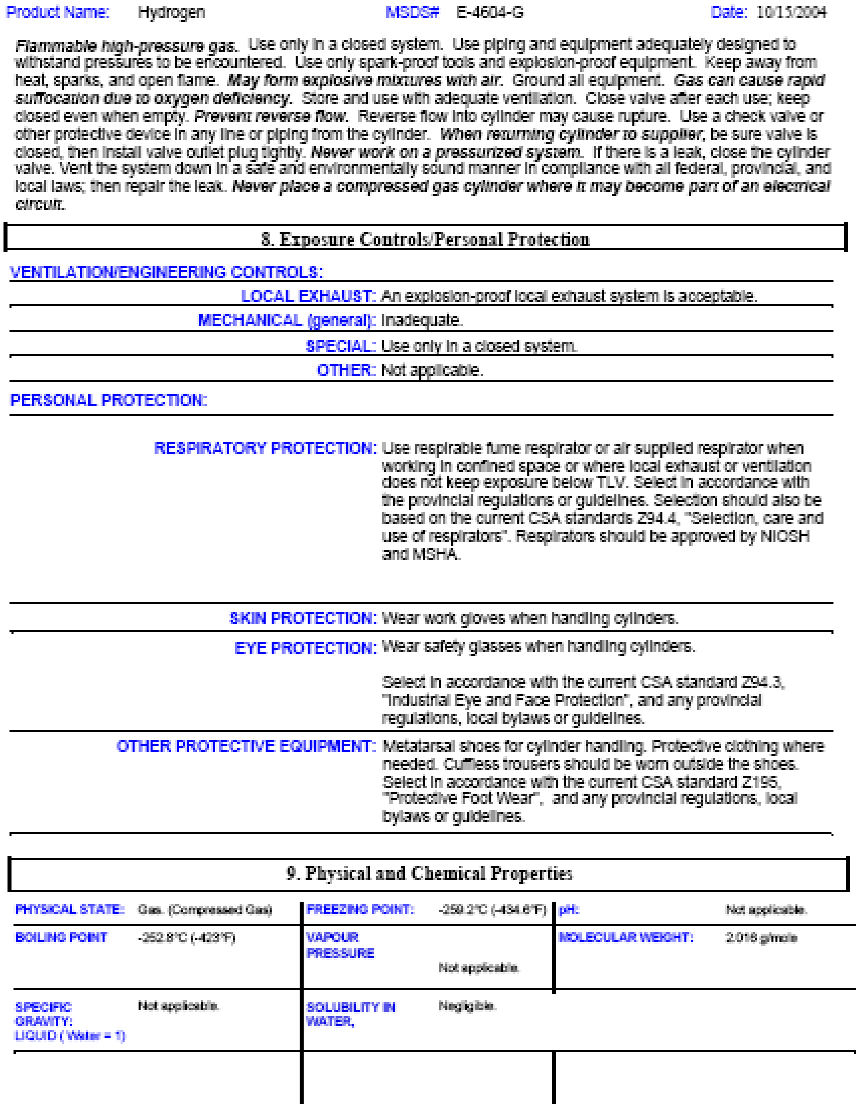
Store and use with adequate ventilation. Separate flammable cylinders from oxygen, chlorine, and other oxidizers by at least 6 m or use a barricade of non-combustible material. This barricade should be at least 1.5 m high and have a fire resistance rating of at least ½ hour. Firmly secure cylinders upright to keep them from falling or being knocked over. Screw valve protection cap firmly in place by hand. Post "No Smoking or Open Flames" signs in storage and use areas. There must be no sources of ignition. All electrical equipment in storage areas must be explosion-proof. Storage areas must meet national electric codes for Class 1 hazardous areas. Store only where temperature will not exceed 52 C. Store full and empty cylinders separately. Use a first-in, first-out inventory system to prevent storing full cylinders for long periods. For full details and requirements, see NFPA 50A, "Standard for Gaseous Hydrogen at Consumer Sites", published by the National Fire Protection Association.

PRECAUTIONS TO BE TAKEN IN HANDLING:

Protect cylinders from damage. Use a suitable hand truck to move cylinders; do not drag, roll, slide, or drop. Never attempt to lift a cylinder by its cap; the cap is intended solely to protect the valve. Never insert an object (e.g., wrench, screwdriver, pry bar) into cap openings; doing so may damage the valve and cause a leak. Use an adjustable strap wrench to remove over-tight or rusted caps. Open valve slowly. If valve is hard to open, discontinue use and contact your supplier. For other precautions, see Section 16.

For additional information on stroage and handling, refer to Compressed Gas Association (CGA) pamphlet P-1, *Safe Handling of Compressed Gases in Containers*, available from the CGA. Refer to Section 16 for the address and phone number along with a list of other available publications.

OTHER HAZARDOUS CONDITIONS OF HANDLING, STORAGE, AND USE:



Product Name: Hydrogen **MSDS#** E-4604-G **Date:** 10/15/2004

Flammable high-pressure gas. Use only in a closed system. Use piping and equipment adequately designed to withstand pressures to be encountered. Use only spark-proof tools and explosion-proof equipment. Keep away from heat, sparks, and open flame. ***May form explosive mixtures with air.*** Ground all equipment. ***Gas can cause rapid suffocation due to oxygen deficiency.*** Store and use with adequate ventilation. Close valve after each use; keep closed even when empty. ***Prevent reverse flow.*** Reverse flow into cylinder may cause rupture. Use a check valve or other protective device in any line or piping from the cylinder. ***When returning cylinder to supplier,*** be sure valve is closed, then install valve outlet plug tightly. ***Never work on a pressurized system.*** If there is a leak, close the cylinder valve. Vent the system down in a safe and environmentally sound manner in compliance with all federal, provincial, and local laws; then repair the leak. ***Never place a compressed gas cylinder where it may become part of an electrical circuit.***

8. Exposure Controls/Personal Protection

VENTILATION/ENGINEERING CONTROLS:

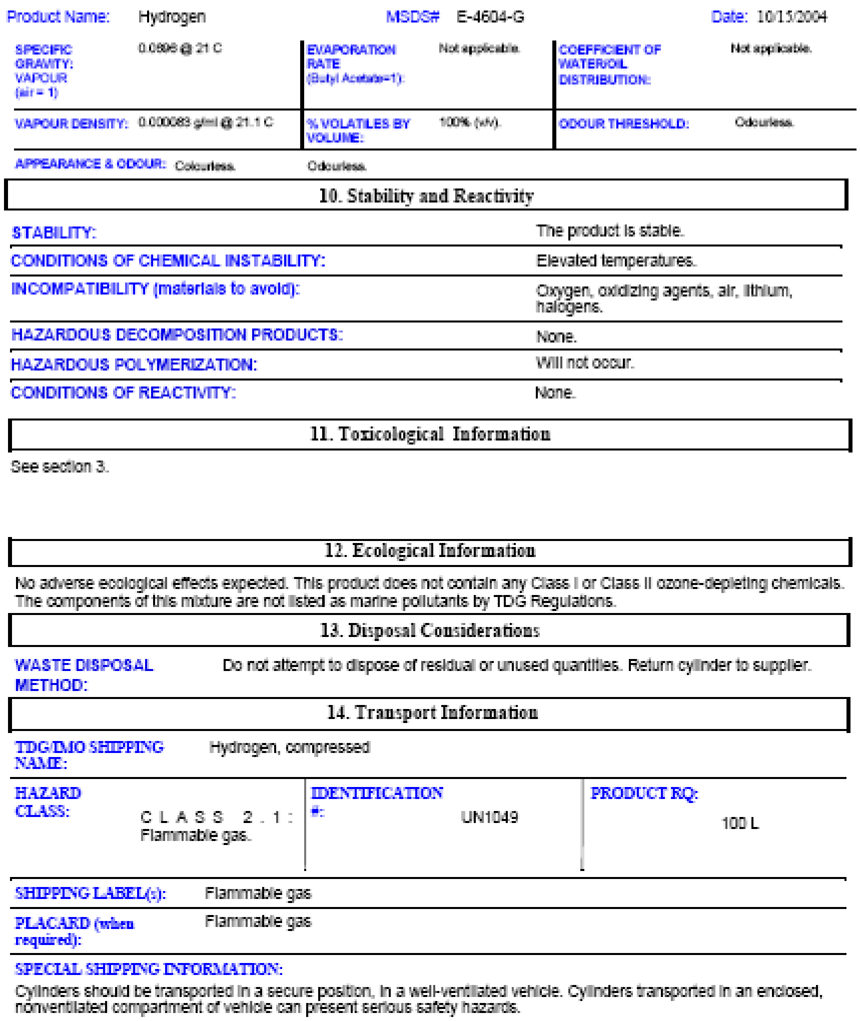
LOCAL EXHAUST:	An explosion-proof local exhaust system is acceptable.
MECHANICAL (general):	Inadequate.
SPECIAL:	Use only in a closed system.
OTHER:	Not applicable.

PERSONAL PROTECTION:

RESPIRATORY PROTECTION:	Use respirable fume respirator or air supplied respirator when working in confined space or where local exhaust or ventilation does not keep exposure below TLV. Select in accordance with the provincial regulations or guidelines. Selection should also be based on the current CSA standards Z94.4, "Selection, care and use of respirators". Respirators should be approved by NIOSH and MSHA.
SKIN PROTECTION:	Wear work gloves when handling cylinders.
EYE PROTECTION:	Wear safety glasses when handling cylinders. Select in accordance with the current CSA standard Z94.3, "Industrial Eye and Face Protection", and any provincial regulations, local bylaws or guidelines.
OTHER PROTECTIVE EQUIPMENT:	Metatarsal shoes for cylinder handling. Protective clothing where needed. Cuffless trousers should be worn outside the shoes. Select in accordance with the current CSA standard Z195, "Protective Foot Wear", and any provincial regulations, local bylaws or guidelines.

9. Physical and Chemical Properties

PHYSICAL STATE:	Gas. (Compressed Gas)	**FREEZING POINT:**	-259.2°C (-434.6°F)	**pH:**	Not applicable.
BOILING POINT	-252.8°C (-423°F)	**VAPOUR PRESSURE**	Not applicable.	**MOLECULAR WEIGHT:**	2.016 g/mole
SPECIFIC GRAVITY: LIQUID (Water = 1)	Not applicable.	**SOLUBILITY IN WATER,**	Negligible.		



Product Name: Hydrogen **MSDS#** E-4604-G **Date:** 10/15/2004

SPECIFIC GRAVITY: VAPOUR (air = 1)	0.0696 @ 21 C	**EVAPORATION RATE (Butyl Acetate=1):**	Not applicable.	**COEFFICIENT OF WATER/OIL DISTRIBUTION:**	Not applicable.
VAPOUR DENSITY:	0.000083 g/ml @ 21.1 C	**% VOLATILES BY VOLUME:**	100% (v/v).	**ODOUR THRESHOLD:**	Odourless.

APPEARANCE & ODOUR: Colourless. Odourless.

10. Stability and Reactivity

STABILITY:	The product is stable.
CONDITIONS OF CHEMICAL INSTABILITY:	Elevated temperatures.
INCOMPATIBILITY (materials to avoid):	Oxygen, oxidizing agents, air, lithium, halogens.
HAZARDOUS DECOMPOSITION PRODUCTS:	None.
HAZARDOUS POLYMERIZATION:	Will not occur.
CONDITIONS OF REACTIVITY:	None.

11. Toxicological Information

See section 3.

12. Ecological Information

No adverse ecological effects expected. This product does not contain any Class I or Class II ozone-depleting chemicals. The components of this mixture are not listed as marine pollutants by TDG Regulations.

13. Disposal Considerations

WASTE DISPOSAL METHOD: Do not attempt to dispose of residual or unused quantities. Return cylinder to supplier.

14. Transport Information

TDG/IMO SHIPPING NAME: Hydrogen, compressed

HAZARD CLASS:	CLASS 2.1: Flammable gas.	**IDENTIFICATION #:**	UN1049	**PRODUCT RQ:**	100 L

SHIPPING LABEL(s): Flammable gas

PLACARD (when required): Flammable gas

SPECIAL SHIPPING INFORMATION:

Cylinders should be transported in a secure position, in a well-ventilated vehicle. Cylinders transported in an enclosed, nonventilated compartment of vehicle can present serious safety hazards.

15. Regulatory Information

The following selected regulatory requirements may apply to this product. Not all such requirements are identified. Users of this product are solely responsible for compliance with all applicable federal, provincial, and local regulations.

WHMIS (Canada)	CLASS A: Compressed gas. CLASS B-1: Flammable gas.

International Regulations

EINECS	Not available.
DSCL (EEC)	This product is not classified according to the EU regulations.
International Lists	No products were found.

16. Other Information

MIXTURES:

When two or more gases, or liquefied gases are mixed, their hazardous properties may combine to create additional, unexpected hazards. Obtain and evaluate the safety information for each component before you produce the mixture. Consult an Industrial Hygienist, or other trained person when you make your safety evaluation of the end product. Remember, gases and liquids have properties which can cause serious injury or death.

HAZARD RATING SYSTEM:

HMIS RATINGS:

HEALTH	**0**
FLAMMABILITY	**4**
PHYSICAL HAZARD	**0**

STANDARD VALVE CONNECTIONS FOR U.S. AND CANADA:

THREADED:	CGA-350
PIN-INDEXED YOKE:	Not available.
ULTRA-HIGH-INTEGRITY CONNECTION:	CGA-703.

Use the proper CGA connections. **DO NOT USE ADAPTERS.** Additional limited-standard connections may apply. See CGA pamphlets V-1 and V-7 listed below.

Ask your supplier about free Praxair safety literature as referred to in this MSDS and on the label for this product. Further information about this product can be found in the following pamphlets published by the Compressed Gas Association, Inc. (CGA), 4221 Walney Road, 5th Floor, Chantilly, VA 20151-2923, Telephone (703) 788-2700, Fax (703) 961-1831, website: www.cganet.com.

AV-1	Safe Handling and Storage of Compressed Gas
G-5	Hydrogen
G-5.3	Commodity Specification for Hydrogen
P-1	Safe Handling of Compressed Gases in Containers
P-14	Accident Prevention in Oxygen-Rich, Oxygen-Deficient Atmosphere
SB-2	Oxygen-Deficient Atmospheres
V-1	Compressed Gas Cylinder Valve Inlet and Outlet Connections
V-7	Standard Method of Determining Cylinder Valve Outlet Connections for Industrial Gas Mixtures
---	Handbook of Compressed Gases, Fourth Edition

PREPARATION INFORMATION:

DATE: 10/15/2004

DEPARTMENT: Safety and Environmental Services
TELEPHONE: 905-803-1600

The opinions expressed herein are those of qualified experts within Praxair Canada Inc. We believe that the information contained herein is current as of the date of this Material Safety Data Sheet. Since the use of this information and the conditions of use of the product are not within the control of Praxair Canada Inc., it is the user's obligation to determine the conditions of safe use of the product.

Praxair Canada Inc. requests the users of this product to study this Material Data Sheet (MSDS) and become aware of product hazards and safety information. To promote safe use of this product, a user should (1) notify its employees, agents and contractors of the information on this MSDS and any product hazards and safety nformation, (2) furnish this same information to each of its customers for the product, and (3) request such customers to notify their employees and customers for the product of the same product hazards and safety information.

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Praxair Canada Inc.

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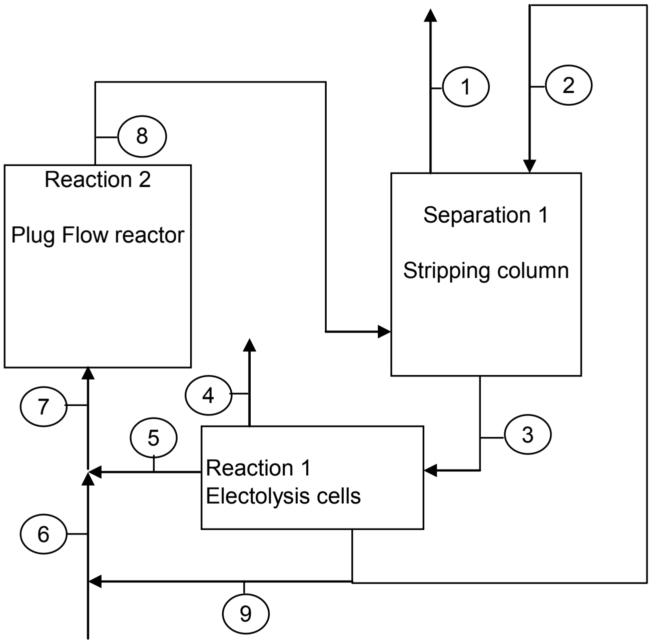
PRAXAIR

Praxair Canada Inc.
1 City Centre Drive
Suite 1200
Mississauga, ON L5B 1M2

10.1 Flow Sheets

Hallett Air Products

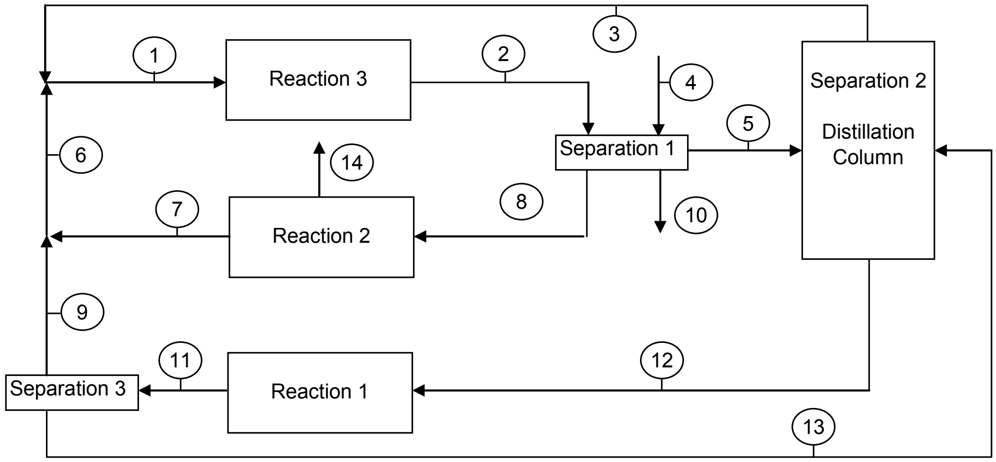


Stream number	1	2	3	4	5	6	7	8	9
Pressure (kpa)	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3
Temp (C)	25	25	19	25	25	25	25	800	25
Flow (kmol/s)	1.43	9.91	16.88	2.85	4.20	3.85	9.05	8.18	1.00
Flow ton/day	**3940**			**500**		**4440**			
Compsition									
HCl	0	0.06	0.40	0	0	0.04	0.01	0.71	0.06
O2	1.00	0	0	0	0	0	0	0.19	0
Cl2	0	0	0	0	1.00	0	0.78	0	0
H2O	0	0.94	0.60	0	0	0.96	0.21	0.10	0.94
H2	0	0	0	1.00	0	0	0	0	0

Reaction 1: **$2HCl \rightarrow Cl_2 + H_2$ (electrolysis)**

Reaction 2: **$Cl_2 + H_2O \rightarrow 2HCl + \frac{1}{2}O_2$**

Sulphur-Iodine Flowsheet



Stream number	1	2	3	4	5	6	7	8	9	10
Pressure (kpa)	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3	101.3
Temp (C)	350	25	100	25	0	570	450	25	850	25
Flow (kmol/s)	12.90	9.67	4.00	2.85	6.00	8.90	3.15	3.00	5.75	1.43
Flow kg/day				**4440**						**3940**
Compsition										
H2SO4	0	0.38	0	0	0.61	0	0	0	0	0
SO2	0.38	0	0	0	0	0.42	0	0	0.79	0
H2O	0.14	0	1.00	1.00	0.39	0.03	0.07	0.15	0	0
O2	0.06	0.05	0	0	0	0.09	0	0	0.21	1.00
HI	0	0.57	0	0	0	0	0	0.80	0	0
I2	0.42	0	0	0	0	0.46	0.93	0.05	0	0
H2	0	0	0	0	0	0	0	0	0	0

Stream number	11	12	13	14
Pressure (kpa)	101.3	101.3	101.3	101.3
Temp (C)	850	35	80	25
Flow (kmol/s)	7.88	3.15	2.13	2.85
Flow kg/day				**500**
Compsition				
H2SO4	0.10	1.00	0.76	0
SO2	0.58	0	0	0
H2O	0.17	0	0.24	0
O2	0.15	0	0	0
HI	0	0	0	0
I2	0	0	0	0
H2	0	0	0	1.00

Reaction 1 $\mathbf{H_2SO_4 \rightarrow SO_2 + H_2O + \frac{1}{2}O_2}$

Reaction 2 $\mathbf{2HI \rightarrow I_2 + H_2}$

Reaction 3 $\mathbf{I_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HI}$

10.2 Tables of Data

Investment Summary

April, 2005

Hallett Air Product Cycle with Transportation & Storage

				TOTAL
Module Costs				
Fabricated Equipment				
Electrolyzer		$143,000,000		
Absorber Tower		$2,802,800		
Heat Exchangers		$657,800		
Distribution Pipes		$335,000,000		
Reactor		$2,255,100		
Total Fabricated Equipment:		**$483,715,700**		
Process Machinery				
Pump		$1,287,000		
Total Process Machinery:		**$1,287,000**		
Storage				
Hydrogen Storage Tanks		$272,000,000		
Total Storage:		**$272,000,000**		
Total Bare Module Costs:				**$ 757,003,000.00**
Direct Permanent Investment				
Cost of Site Preparation:		$37,850,200		
Cost of Service Facilities:		$37,850,200		
Allocated Costs for utility plants and related facilitie		$0		
Direct Permanent Investment:				**$ 832,703,000.00**
Total Depreciable Capital				
Cost of Contigencies and Contractor Fees:		$149,886,500		
Total Depreciable Capital:				**$ 982,590,000.00**
Total Permanent Investment				
Cost of Land:		$19,651,800		
Cost of Royalties:		$0		
Cost of Plant Start-Up:		$98,259,000		
Total Permanent Investment:				**$ 1,100,501,000.00**
Working Capital				
Inventory				
Hydrogen	⇨ 500,000 kg		$2,375,000	
Water	⇨ 4,500,000 kg		$2,700	
Chlorine	⇨ 1,000 kg		$200	
Total Inventory:			**$2,377,900**	
Accounts Receivable:			$2,638,900	
Cash Reservces:			$1,723,800	
Accounts Payable:			$96,200	
Total Working Capital:			$6,836,800	
TOTAL CAPITAL INVESTMENT				**$ 1,107,337,800.00**

Figure 13: Total Capital Investment for Hallett Air Product Plant

Variable Cost Summary

April, 2005

Hallett Air Product Cycle with Transportation & Storage

		Per kg Hydrogen		TOTAL
Raw Materials				
	Water	$0.01 per kg of Hydrogen	$1,095,000	
	Chlorine	$0.00 per kg of Hydrogen	$75,000	
	Total Raw Materials:	**$0.01 per kg of Hydrogen**	**$1,170,000**	**$ 1,170,000.00**
Utilties				
	Cooling Water	$0.00 per kg of Hydrogen	$176,300	
	Electricity	$1.74 per kg of Hydrogen	$353,046,300	
	Thermal Energy	$0.28 per kg of Hydrogen	$57,651,800	
	Total Raw Materials:	**$2.03 per kg of Hydrogen**	**$410,874,300**	**$ 412,044,300.00**
Byproducts				
	Oxygen	$0.00 per kg of Hydrogen	$0	
	Total Byproducts:	**$0.00 per kg of Hydrogen**	**$0**	**$ 412,044,300.00**
General Expenses				
	Selling / Transfer:	$0.14 per kg of Hydrogen	$28,895,800	
	Direct Research:	$0.23 per kg of Hydrogen	$46,233,300	
	Allocated Research:	$0.02 per kg of Hydrogen	$4,816,000	
	Administrative Expense:	$0.10 per kg of Hydrogen	$19,263,900	
	Management Incentives:	$0.06 per kg of Hydrogen	$12,039,900	
	Total Byproducts:	**$0.55 per kg of Hydrogen**	**$111,249,000**	**$ 523,293,300.00**
TOTAL		**$2.58 per kg of Hydrogen**	**$523,293,300**	**$ 523,293,300.00**

Figure 14: Variable Cost for the Hallett Air Product Plant

Fixed Cost Summary

April, 2005

Hallett Air Product Cycle with Transportation & Storage

			TOTAL
Operations			
	Direct Wages and Benefits:	$3,120,000	
	Direct Salaries and Benefits:	$468,000	
	Operating Supplies and Services:	$187,200	
	Technical Assistance to Manufacturing:	$0	
	Control Laboratory:	$0	
	Total Operations:	**$3,775,200**	**$ 3,775,200.00**
Maintenance			
	Wages and Benefits:	$44,216,550	
	Salaries and Benefits:	$11,054,138	
	Materials and Services:	$44,216,550	
	Maintenance Overhead:	$2,210,828	
	Total Maintenance:	**$101,698,066**	**$ 105,473,266.00**
Operating Overhead			
	General Plant Overhead:	$4,178,967	
	Mechanical Department Services:	$1,412,609	
	Employee Relations Department:	$3,472,663	
	Business Services:	$4,355,543	
	Total Operating Overhead:	**$13,419,782**	**$ 118,893,048.00**
Property Insurance and Taxes			
	Total Property Insurance and Taxes:	**$19,651,800**	**$ 138,544,848.00**
TOTAL			**$ 138,544,848.00**

Figure 15: Fixed Cost for the Hallett Air Product Plant

Investment Summary

April, 2005

Sulphur Iodine Cycle with Transportation & Storage

			TOTAL
Bare Module Costs			
Fabricated Equipment			
Reactor		$429,000,000	
Distribution Pipes		$335,000,000	
Total Fabricated Equipment:		**$764,000,000**	
Storage			
Storage Tanks		$272,000,000	
Total Storage:		**$272,000,000**	
Total Bare Module Costs:			**$ 1,036,000,000.00**
Direct Permanent Investment			
Cost of Site Preparation:		$51,800,000	
Cost of Service Facilities:		$51,800,000	
Allocated Costs for utility plants and related facilitie		$0	
Direct Permanent Investment:			**$ 1,139,600,000.00**
Total Depreciable Capital			
Cost of Contigencies and Contractor Fees:		$205,128,000	
Total Depreciable Capital:			**$ 1,344,728,000.00**
Total Permanent Investment			
Cost of Land:		$26,894,600	
Cost of Royalties:		$0	
Cost of Plant Start-Up:		$134,472,800	
Total Permanent Investment:			**$ 1,506,095,000.00**
Working Capital			
Inventory			
Hydrogen	⇨ 500,000 kg	$2,375,000	
Water	⇨ 4,500,000 kg	$2,700	
Total Inventory:		**$2,377,700**	
Accounts Receivable:		$2,638,900	
Cash Reservces:		$1,700,300	
Accounts Payable:		$90,000	
Total Working Capital:		$6,806,900	
TOTAL CAPITAL INVESTMENT			**$ 1,512,901,900.00**

Figure 16: Total Capital Investment for the Sulphur Iodine Plant

Variable Cost Summary

April, 2005

Sulphur Iodine Cycle with Transportation & Storage

		Per kg Hydrogen		TOTAL
Raw Materials				
	Water	$0.01 per kg of Hydrogen	$1,095,000	
	Total Raw Materials:	**$0.01 per kg of Hydrogen**	**$1,095,000**	**$1,095,000**
Utilties				
	Cooling Water	$0.06 per kg of Hydrogen	$13,167,400	
	Thermal Energy	$1.53 per kg of Hydrogen	$310,843,100	
	Total Raw Materials:	**$1.60 per kg of Hydrogen**	**$324,010,500**	**$325,105,500**
Byproducts				
	Oxygen	$0.00 per kg of Hydrogen	$0	
	Total Byproducts:	**$0.00 per kg of Hydrogen**	**$0**	**$325,105,500**
General Expenses				
	Selling / Transfer:	$0.14 per kg of Hydrogen	$28,895,800	
	Direct Research:	$0.23 per kg of Hydrogen	$46,233,300	
	Allocated Research:	$0.02 per kg of Hydrogen	$4,816,000	
	Administrative Expense:	$0.10 per kg of Hydrogen	$19,263,900	
	Management Incentives:	$0.06 per kg of Hydrogen	$12,039,900	
	Total Byproducts:	**$0.55 per kg of Hydrogen**	**$111,249,000**	**$436,354,500**
TOTAL		**$2.15 per kg of Hydrogen**	**$436,354,500**	**$436,354,500**

Figure 17: Variable Cost for the Sulphur Iodine Plant

Fixed Cost Summary

April, 2005

Sulphur Iodine Cycle with Transportation & Storage

			TOTAL
Operations			
	Direct Wages and Benefits:	$3,120,000	
	Direct Salaries and Benefits:	$468,000	
	Operating Supplies and Services:	$187,200	
	Technical Assistance to Manufacturing:	$0	
	Control Laboratory:	$0	
	Total Operations:	**$3,775,200**	**$ 3,775,200.00**
Maintenance			
	Wages and Benefits:	$60,512,760	
	Salaries and Benefits:	$15,128,190	
	Materials and Services:	$60,512,760	
	Maintenance Overhead:	$3,025,638	
	Total Maintenance:	**$139,179,348**	**$ 142,954,548.00**
Operating Overhead			
	General Plant Overhead:	$5,625,255	
	Mechanical Department Services:	$1,901,495	
	Employee Relations Department:	$4,674,508	
	Business Services:	$5,862,942	
	Total Operating Overhead:	**$18,064,200**	**$ 161,018,748.00**
Property Insurance and Taxes			
	Total Property Insurance and Taxes:	**$26,894,560**	**$ 187,913,308.00**
TOTAL			**$ 187,913,308.00**

Figure 18: Fixed Cost for the Sulphur Iodine Plant

Roadway Delivery of H_2

	Units	Data	Results	
Production Rate	lb/hr	**41666.67**		
Annual Production	tons/day	500		
Annual Production	lb/year	365,242,167		
Delivery Distance (one-way)				
From **Hartsville** to				
Columbia, SC	miles	73.38		
Charlotte, NC	miles	126.32		
Raleigh, NC	miles	60.77		
Delivery Distance (two-way)				
From **Hartsville** to				
Columbia, SC	miles	146.77		
Charlotte, NC	miles	252.65		
Raleigh, NC	miles	121.54		
Total Miles Driven for year		521	**190,149**	mi/yr
Delivery Distance (Time per Trip)				
From **Hartsville** to				
Columbia, SC	miles	146.77	2.26	hr/trip
Charlotte, NC	miles	252.65	3.89	hr/trip
Raleigh, NC	miles	121.54	1.87	hr/trip
Total Time per Trip			**8.01**	hr/trip
Number of Trips per Year	trips/yr		1,240,039	
Total Drive Time	hr/year		9,938,562	
Load/Unload Time	hr/year		930,029	
Total Delivery Time	hr/year		9,938,570	
Trucks Required	Trucks		**2494**	
Annual Fuel Use	gal		31,692	
Total Capital Cost	$		623,500,000	
Depreciation	$ (annually)		122,621,667	
Annual Fuel Cost	$ (annually)		72,574	
Annual Labor Cost	$ (annually)		285,733,898	
Total Annual Cost	$ (annually)		**408,428,138**	

Trucking Assumptions

Truck Size	lb	882
Cost of Tube Tanker Truck	$	100000
Truck Mileage	mi/gal	6
Truck Speed	mi/hr	65
Truck Load Time	hr	0.75
Truck Availability	hr/year	8766
Driver Wage	$/hr	28.75
Driver Availability	hr/year	4383
Diesel Price	$/gal	2.29
Truck BOR	%/day	0.3
Truck Under Cost	$	60000
Truck Cab Cost	$	90000
Trailer Dep	yr	6
Tractor Dep	yr	4

Table 9 Data used to calculate number of Tube Trailers

10.3 Costs of Electrolyzer

Shell Cost for the Electrolizer

We found a similar process, producing chlorine from HCl. We based our calculation on that.*
*<HClelectrolysisspecifics.pdf>

Area

175	m2 per unit
111,781	total m2 of electrode needed

Electrode Dimensions

length	4	m
width	0.25	m
thickness	0.003	m
total area per strip	2.02	m^2

# of electrode

$\frac{\text{total area of electrode}}{\text{total area per strip}}$	55,337	electrode

# of electrode per Cell

100 electrode	553	Cell

Volume of each Cell

Spacing between electrodes	0.05	m
thickness	0.025	m
length	7.55	m
Height	5	m
width	1.50	m
Total Volume per cell	57	m^3

Surface area of the shell

5 sides	102	m^2
total area for all cell	56,347	m^2

Assuming that the thickness of the stainless steel sheet is 6.35 mm

the total volume is	358	m^3
density of 304 SS	7,850	kg / m^3
mass of 304 SS	2,809	tonnes
cost of 304 SS per ton	$2,900	
Total cost of 304 SS	**$ 8,145,418**	

Table 10 Shell Cost for the Electrolyzer

Electrode Cost for the Electrolizer

# of electrode per Cell

100 electrode 553 Cell*

* for the Hydrogen only. So using the same number for the anode

Total # of electrodes per Cell

200

Total # number of electrodes needed

110,675

Cost of each electrode*

$400

Total cost of electrodes

$ 44,269,802

Total cost for the electrolizer

$ 52,415,220

Plus the cost of installation and other costs **$ 168,252,857**

* the cathode in Ni and the anode is made of Ti <TP_electrolyse.pdf>

Table 11 Electrode Cost for the Electrolyzer

Storage Tank Cost

Density of hydrogen

30 kg / m3 from PROII

seven days storage inventory

500,000 kg

total tank volume needed

16,706 m3

Number of tanks if each one is 20,000 m3

1 tanks

Diameter, m	Length, m	Volume, m3
4	54	675

Number of tanks if each one is 675 m3

25 tanks

Total Cost for the Storage Tanks

6,912,081

$ 171,114,951

Table 12 Total Cost for One Day of Storage of Hydrogen

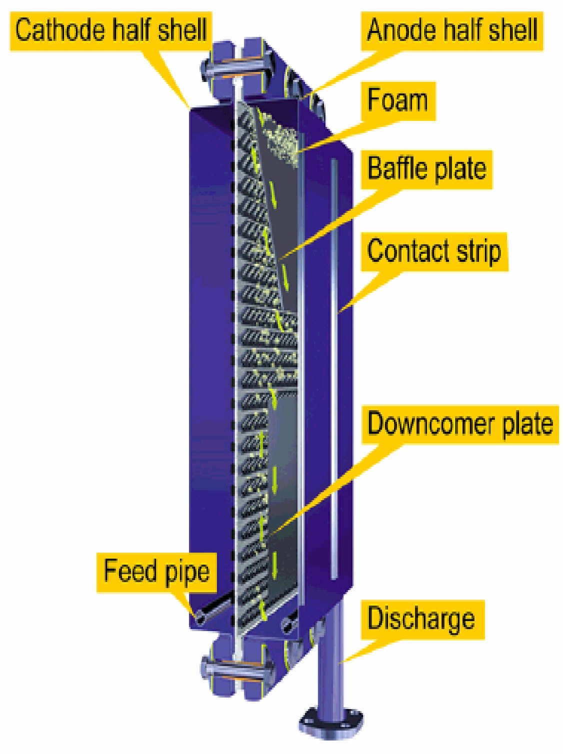


Figure 19: Electrolysis Element

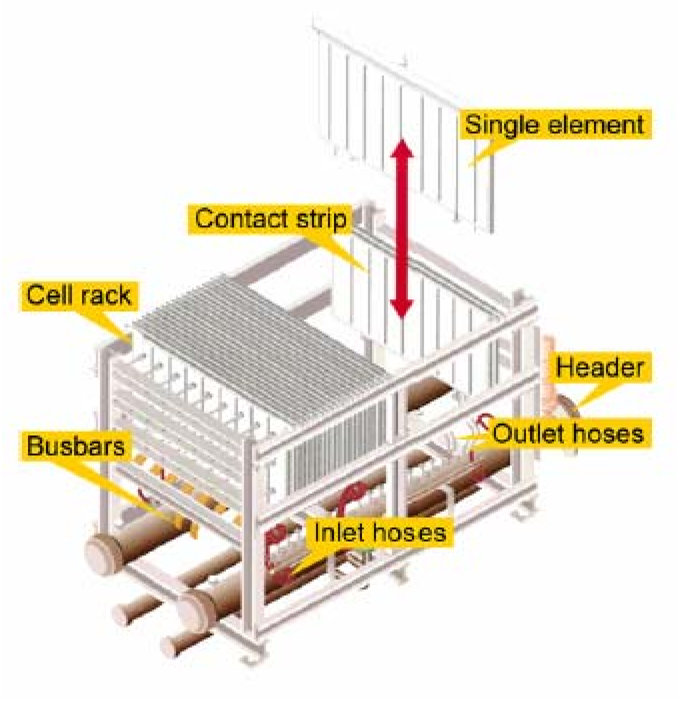


Figure 20: Electrolysis Cell

10.4 References

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