Sulfur Iodine Process Summary
For the
Hydrogen Technology Down-Selection:
Process Performance Package

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Summary

This document describes the details of implementing a Sulfur-Iodine (S-I) hydrogen production plant to deploy with the Next General Nuclear Power Plant (NGNP). Technical requirements and specifications are included, and a conceptual plant design is presented. The following areas of interest are outlined in particular as a baseline for the various technology comparisons:

- Performance Criteria
    - Quantity of hydrogen produced
    - Purity of hydrogen produced
    - Flexibility to serve various applications
    - Waste management

- Economic Considerations
    - Cost of hydrogen
    - Development costs

- Risk
    - Technical maturity of the S-I process
    - Development risk
    - Scale up options

Discussion

General Atomics (GA) has been developing and evaluating the S-I process since inventing the cycle in the 1970's. It has become the most widely studied thermochemical water-splitting cycle in the world. There has been extensive technical and economic analyses done both within GA and elsewhere to examine the potential viability of the process. As DOE moves toward a down-select decision for implementing a hydrogen technology with NGNP, it may be interesting to note that three other countries are engaging in roughly similar efforts.

France has ongoing research activities for each of the hydrogen technologies under consideration for the DOE down-select. However, indications are that France will implement low-temperature alkaline electrolysis on a large scale before any of the developing technologies come to maturation. With the very high percentage (~80%) of electricity in France already supplied by pressurized water reactors, electrolysis is an attractive option. Peak capacity exceeds demand, and France is a large exporter of electricity. With inexpensive and excess electricity available, and the use of electrolysis to level this resource, France can potentially implement low-temperature electrolysis under favorable economic terms.

Both Japan and the Republic of Korea (ROK) have substantial programs in place to develop thermochemical water splitting for production of hydrogen using High-Temperature Gas-Cooled Reactors (HTGRs). Both countries have selected S-I as the

technology for implementation. The U.S. has been developing thermochemical water splitting as part of the Nuclear Hydrogen Initiative (NHI). All three countries have demonstrated thermochemical water splitting at the laboratory scale. In December 2008, the ROK Atomic Energy Commission officially approved nuclear hydrogen development as a national program, with the development of key and basic technologies through 2017 and the goal of demonstrating nuclear hydrogen production using the S-I process and a Very High Temperature Reactor (VHTR) by 2026. The Japan Energy Basic Plan includes a chapter for hydrogen energy utilization, with the goal of commercialization of hydrogen production systems using nuclear energy and other non-fossil fuel sources. To that end, the Japan Atomic Energy Agency (JAEA) has built the 30 MW(t) High Temperature Engineering Test Reactor (HTTR) and has an active plan for demonstrating hydrogen production using S-I thermochemical water splitting at an engineering scale with heat supplied by the HTTR. The HTTR has successfully produced process heat at 950°C and the design includes an installed heat exchanger manufactured from very high temperature materials for coupling the HTTR to the hydrogen production plant. Under the NHI, General Atomics (GA) has collaborated with Sandia National Laboratory and the CEA of France to build and operate a laboratory-scale loop for thermochemical water splitting at prototypical temperatures and pressures.

Both Japan and the ROK have expressed a strong interest in collaborating with the U.S. for further development of S-I thermochemical water splitting for hydrogen production. In August 2005, a Memorandum of Understanding (MOU) was signed between San Diego-based General Atomics (GA) and the Korea Atomic Energy Research Institute (KAERI), which included establishing Nuclear Hydrogen Joint Development Centers (NHJDC) in both San Diego and Daejeon, Korea. As part of this MOU, GA has provided support for the ROK nuclear hydrogen program. GA has also enjoyed a close relationship with JAEA on HTGR and hydrogen production design and technology development, and GA is currently working with Idaho National Laboratory and JAEA for utilization of the HTTR and other JAEA facilities to support NGNP technology development. In May 2009, a trilateral meeting was held among GA, KAERI, and JAEA, and all parties agreed to collaborate on development of S-I thermochemical water splitting and other nuclear heat applications. The U.S. would benefit substantially from international collaboration with Japan and the ROK on development of nuclear hydrogen production, particularly with regard to cost sharing provided by Japan and the ROK on materials and component development, pilot-scale demonstration, and engineering-scale demonstration.

NGNP Hydrogen Plant Design

Idaho National Laboratories (INL) has provided guidelines/specifications for the NGNP hydrogen plant. Although the NGNP reactor core type has not been specified, the reference design includes:

- Up to 600 MWt per reactor unit
- 750 to 800°C Initial Reactor Outlet Temperature

- 7MPa Reactor Outlet Pressure

- Helium Primary Coolant

- Graphite Moderated

- Pebble-Bed or Prismatic Reactor Core

- 60-year Design Life

- Scheduled Startup 2021.

Although future reactor outlet temperatures could be as high as 950°C, this evaluation will be based on initial startup temperatures of 750 to 800°C. The hydrogen production technology will interface with the NGNP via an intermediate heat exchanger (IHX) or steam generator. The interface parameters are as follows:

- Utilize up to 50 MWt total reactor power with any electric conversion at 40%

- He IHX outlet to the hydrogen process at 700°C and 7 MPa pressure (for SI and HyS)

- Steam outlet temperature from generator at 550°C at 15 MPa pressure (for HTE)

- Assume no contaminants are introduced at or upstream of this interface.

To this end, GA has assembled a conceptual design for a NGNP S-I plant utilizing 50 MWt of reactor heat, plus additional electricity. GA has worked closely with CEA over the last two years to analyze process flowsheets and to determine the source of any differences in thermal efficiency. Each party has used different thermodynamic models, and different concepts for interfacing the hydrogen process with the nuclear heat source. The goal was to determine a common design, if possible, for a S-I hydrogen plant. The result of this analysis is the set of process flowsheets presented in this design for NGNP. The process flowsheets and stream tables are found in Appendix A.

A technical summary of the design and predicted performance is as follows:

- 50 MWt and 7.5 MWe are required for plant operation at full capacity. The energy requirement is distributed as shown in Table 1:

Table 1. NGNP S-I Energy Consumption Per Mole Hydrogen

Section	Q (kJt/mol)	W (kJe/mol)	W (kJt/mol eq)	Total Thermal eq (kJt/mol)
Bunsen	0	3.9	9.8	9.8
H_2SO_4 Decomposition	364.0	0*	0	358.8
HI Decomposition	182.0	77.9	194.8	374.2
Total	**546.0**	**81.8**	**204.5**	**742.7**

* Power generated in the HI decomposition section provides electrical power to the H_2SO_4 decomposition section

- The quantity of hydrogen produced at full capacity is 15,950 kg/day at a pressure of 120 bar (1,740 psi)

- The thermal efficiency of the hydrogen plant is calculated using the formula below:

$$\eta = \frac{\Delta H^0_{H_2O}(T = 25°C)}{Q + \dfrac{W}{\eta_{el}}}$$

$$\eta = 100 \times \frac{HHV\ H_2}{Q + W/0.4} = \frac{286}{546 + 81.8/0.4} = 38.1\%$$

The high heating value (HHV) of hydrogen is 286 kJ/mole, and the low heating value (LHV) is 242 kJ/mole. Using 40% as the electrical conversion efficiency, the energy consumption shown in Table 1 leads to thermal efficiencies of 38.1% (HHV) and 32.4% (LHV).

This efficiency includes all shaft work for pumps and compressors.

Purity of Hydrogen Produced and Flexibility to Serve Various Applications

Potential contaminates for hydrogen in the product stream are water, HI, and iodine. HI and iodine are readily washed from hydrogen streams, and hydrogen can be separated from water as the vapor product in the same wash column. Predicted hydrogen purity (mole percent) is 99.953%. Water largely makes up the remainder at 0.047%. No detectable HI is present and iodine concentration is on the order of 10^{-8}. Additional steps to further reduce the water content can be taken if the NGNP product hydrogen is primarily designated for very high purity (>99.99%) applications like fuel cells. Applications such as refining, Fischer-Tropsch synthesis, methanol synthesis, synthetic natural gas production, ammonia and its derivatives, float glass manufacturing, and food use should all be possible with the predicted hydrogen purity.

Waste Management

Waste management is not a major issue for any of the hydrogen technologies under consideration. Each is designed as a closed loop system, with no major waste streams designed into the process. For S-I, there may be periodic blowdown required, but work at lab-scale has not resulted in accumulation of detectable contaminants that allows for quantification of volume or frequency of waste discharges. The two product streams each have low levels of contaminants that can be noted. The oxygen product stream from

the Bunsen reaction is predicted to contain approximately 10 ppmv sulfur dioxide. This discharge is equivalent to 2.8 kg/day, which is likely to be well within regulatory standards. The hydrogen stream carries a small amount of iodine (~15 ppbv) that is equivalent to less than 50 grams discharged per day.

Economic Considerations

The cost of hydrogen is an important parameter in any analysis of a particular process. For S-I, estimates over the years have ranged from near $2/kg to over $10/kg. Clearly, large uncertainties exist in the various estimates. Typically, the lower estimates stem from an nth-of-a-kind analysis with a startup in the 2020-2030 timeframe. First-of-a-kind estimates with present day costing lead to higher cost predictions. A recent work for NGNP by the Westinghouse/PBMR/Shaw Team was an attempt to make a technical and economic assessment of the three candidates technologies, including S-I. The intent was to evaluate the technologies on a consistent basis. Although GA was asked to submit input to the Shaw team, the flowsheets and process design used in the study were generated by Shaw. As a result, major process changes were implemented that had significant impact on the economic calculations.

A study undertaken by Technology Insights (TI) provided some insight into the potential uncertainties contained within, but not explicitly addressed by, the Shaw work. Estimates for energy costs, escalation of energy costs, and costs for engineering materials in the Shaw report were based on 3rd quarter 2008 prices, near the peak of the commodities "bubble" that occurred last year. The TI analysis showed that the cost of hydrogen could look different with a more levelized analysis of the cost of energy. For the work in this data package, GA has attempted to be consistent with the Shaw report on the capital costing of most equipment, but varies from Shaw in the following ways:

- The flowsheet design is consistent with previously published work by GA and CEA, in that the overall efficiency is near 40% (HHV), rather than under 25% as seen in the Shaw report.

- This work assumed a lower cost for piping and valves compared to Shaw, as it is unnecessary to use tantalum linings everywhere in the plant. Glass or PTFE linings will be used where temperatures are low enough. This correction to the Shaw analysis results in a large effect, as it lowers the overall capital cost by about 30%.

- Shaw assumed an electricity cost of $75/kW-hr, with 1% escalation. We have taken a similar approach to one alternative looked at by TI. Here, we have used the 2008 US average cost of industrial electricity ($63.40/kW-hr) that is posted on the EIA website, with no escalation.[1]

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[1] http://www.eia.doe.gov/cneaf/electricity/epm/table5_6_b.

- The cost of nuclear heat has been assumed in this report to be $20/MW-hr, in line with the 2007 TI Nuclear Hydrogen Initiative report, as opposed to $30/MW-hr in the Shaw report.

The TI reports outline sensitivity to the various cost factors for all three technologies under consideration. In calculations for hydrogen cost in this report, all standard default financial assumptions within H2A have been utilized, with the exception that 2008 costs, not 2005 costs, are calculated.

Cost of Hydrogen

Table 2 below is the GA summary of the estimated cost of hydrogen for the NGNP 50 MW plant, using H2A costing methodology. For comparison, Table 3 is the cost summary for hydrogen published in the Shaw report.

Table 2. GA Cost Estimate Details for an S-I Hydrogen Plant for NGNP

Cost Component	Cost Contribution ($/kg)	Percentage of H2 Cost
Capital Costs	$6.01	65.0%
Fixed O&M: Labor, Taxes, Insurance, Annual Licensing, Permits and Fees, Material Costs for Maintenance And Repairs, Nuclear Decommissioning Funding, Helium Make-up	$0.53	5.7%
Variable O&M: Process Catalyst and Chemical Consumption and Waste Disposal	$0.38	4.1%
Nuclear Heat	$1.50	16.2%
Electric Power	$0.72	7.8%
Process and Cooling Water	$0.11	1.2%
Byproduct Credit (O2)	$0.00	0.0%
Total	**$9.25**	100%

Table 3. Cost Estimate Details for an S-I Hydrogen Plant from the Shaw Report

Cost Component	Cost Contribution ($/kg)	Percentage of H2 Cost
Capital Costs	$4.23	40%
Fixed O&M: Labor, Taxes, Insurance, Annual Licensing, Permits and Fees, Material Costs for Maintenance And Repairs, Nuclear Decommissioning Funding,	$0.70	7%

Helium Make-up		
Variable O&M: Process Catalyst and Chemical Consumption and Waste Disposal	$0.60	6%
Nuclear Heat	$3.21	30%
Electric Power	$2.22	21%
Process and Cooling Water	$0.11	1%
Byproduct Credit (O2)	-$0.38	-4%
Total	**$10.69**	100%

The significant differences between the two summaries are higher capital costs per kg of hydrogen and lower costs of energy for the GA NGNP case. Regarding capital costs, this is primarily economies of scale. An advantage touted by proponents of S-I is the "scaling by volume" characteristic it shares with commercial chemical and petrochemical plants. Economics become more favorable as plant size increases. The Shaw report makes this point as well. However, as plant size decreases, cost per unit of hydrogen increases. A 50 MWt plant is small in comparison to designs at 600 MWt and 2400 MWt that have been done previously, and more favorable economics are difficult to achieve at this lower power level.

Another factor which influences capital cost for the NGNP case is the potential for hydrogen process heat temperature to be as low as 700ºC. With efficient heat recovery in the sulfuric acid decomposition section, process efficiency is not largely affected as the temperature decreases. What does increase significantly is the amount of recycle within the decomposition loop. Thus, component sizes in this section increase. There is no economy of scale advantage in this case, and a penalty of higher capital cost per kg is incurred with lower peak process temperature. A small-scale, low-temperature plant may be implemented with NGNP for technical evaluation, but economic factors under these conditions are not optimized.

Development Costs

As part of the "NGNP Technology Development Road Mapping Report" (GA Document PC-000580), a development plan for the sulfur iodine process has previously been published. The following analysis describes the development plan for the progression of work from TRL 5 through TRL 8. The development to complete TRL 5 will be presented in the next section on Development Risk.

A plan consisting of 3 scale up stages has been developed for the demonstration of the sulfur iodine process on a demonstration nuclear reactor. Table 4 summarizes the progression.

Table 4. Summary of SI development plan

Plant Size	H_2 Production	Performance Criteria
Pilot Plant (70 kW, TRL 6)	20,000 l/hr (0.25 moles/sec)	1000 hrs operating time 1000 hrs catalyst life
Engineering Scale (1.5 MW, TRL 7)	425,000 l/hr (5.3 moles/sec)	2500 hrs operating time 2500 hrs catalyst life
Prototype Plant (50 MW, TRL 8)	8,064,000 l/hr (100 moles/sec)	25,000 hrs operating time 2500 hrs catalyst life

Test Program to Advance Technology Readiness Level (TRL)

Test Objective

The objective of the test will be to design, construct and operate a test plant at the respective power levels. Each of the three sections, Bunsen reactor, H_2SO_4 Decomposition, and HI Decomposition will be scaled up from the previous experiment. Successful testing of the plant will result in the advancement to the next TRL for the SI process.

Test Conditions

The plant will operate under the same process conditions as expected in full-scale facilities. Pressures, temperatures, materials of construction, and composition of process streams will all match design parameters for a full-scale plant.

Test Configuration/Set-up

TRL 6 & 7
The plant will be electrically powered, with no nuclear power plant interface. Some heat integration between sections may be attempted.

TRL 8
The plant will be coupled to the NGNP nuclear heat source. Extensive heat integration to maximize thermal efficiency will be included in the design.

Proposed Test Location

A national laboratory site would be most suitable for location of the pilot plant. INL and SNL are recommended as primary candidates. Capabilities at the national laboratories for conducting hydrogen plant testing include:
- Facilities and resources for conducting long-term testing
- Analytical equipment for product and effluent characterization
- On-site engineering support
- On-site grinding, polishing, welding, shearing, machining, sawing

Pilot Plant Test Measured Parameters

The following parameters would be included in the evaluation of the performance of the pilot plant:

- Length of runs
- Number of runs
- Acid purities exiting Bunsen section
- Consistency or variation in production rates from each section
- Quantity and composition of waste products
- Catalyst life
- Hydrogen flowrates
- Hydrogen purity
- Hydrogen outlet pressure

Data Requirements

Instruments for data capture shall be calibrated and certified for use under the GA ISO 9001 Quality Assurance Level II program, or under an equivalent method. Required accuracy for each device or method shall be determined during the design phase of the development plant program.

Test Evaluation Criteria

Table 5 outlines preliminary criteria for evaluation of pilot plant performance.

Table 5. Pilot Plant Performance Criteria

Sulfur-Iodine Pilot Plant Performance Criteria	
Minimum dispensing pressure (psig)	300
% Hydrogen	> 98%
CO_2 (ppm)	< 100
CO (ppm)	< 1
Sulfur (ppb)	< 10
Ammonia (ppm)	< 1
Non-methane hydrocarbons (ppm)	< 100
Total of Oxygen, Nitrogen and Argon (%)	< 2
Water (ppm)	< 100

Supplementary Tests

Supplemental tests on auxiliary equipment, such as pumps or heat exchangers, may be conducted as necessary to determine parameters such as life cycle and corrosion resistance. Controls systems will be evaluated for safety and effectiveness.

Development Cost and Schedule

The development test program for the HPS must be integrated with the design and fabrication effort for the MHTGR program to assure that conceptual design, final design, production hardware, etc., are available in a timely fashion. This document assumes a test program will arise, with adequate design and development funding, for completion of development testing prior to the start of fabrication. However, all work is subject to DOE contract award and may be supplied or performed by other selected vendors. Completing the test program, described herein, will provide greater confidence in the design prior to the release for fabrication.

Cost

Table 6 below is a summary of estimated costs for development of the SI cycle from TRL 6 to TRL 8 upon the successful operation of the prototype plant at NGNP.

Table 6. Costs Estimates for SI-Based HPS Testing

Test Category	Test	Test Costs ($M)[1]
Pilot Plant	Bunsen Reaction Section	$20.0
	Sulfuric Acid Decomposition Section	$12.1
	Hydriodic Acid Decomposition Section	$23.2
Engineering Demonstration Plant	Bunsen Reaction Section	$31.9
	Sulfuric Acid Decomposition Section	$22.6
	Hydriodic Acid Decomposition Section	$26.5
Prototype Plant	Bunsen Reaction Section	$58.9
	Sulfuric Acid Decomposition Section	$42.6
	Hydriodic Acid Decomposition Section	$80.2
	Total:	$318

[1] In 2005 dollars.

These cost estimates are preliminary and include installation, labor, engineering, and operating costs. Components were individually sized for the relevant scales and the capital cost for each component was calculated using the method of Guthrie (Guthrie, KM, Capital cost estimating, Chemical Engineering, March 24, 1969, 114-142).

Two factors have the potential to significantly reduce development costs. First, there is an effort to obtain more complete thermodynamic data for the chemistries in the hydriodic acid (HI) decomposition section. Initial work done at CEA in 2007 suggests that energy requirements for vaporizing mixtures containing HI are overestimated with current thermodynamic models. If this can be confirmed with further experimental work, it could potentially eliminate costly vapor recompression equipment required for energy recovery in the HI decomposition section. This equipment comprises the single largest capital cost contributor for a SI plant at this time. Electrical demand for the cycle would drop by an order of magnitude or more. This would also significantly reduce hydrogen production costs in a commercial scale plant. HPS DDN HPS-HID-02 describes the requirement for further work in this area.

Second, preliminary discussions have been held between GA and the Japan Atomic Energy Agency (JAEA) regarding development of a SI plant, on the scale of the NGNP prototype that would be coupled to the High Temperature Test Reactor (HTTR) currently operating in Japan. This gas reactor has achieved operation at up to 950ºC. It may be possible for DOE to share development costs for the cycle through a collaborative effort with JAEA in this area. Development times would likely be reduced, as the reactor is already operating.

Schedule

To satisfy an NGNP plant start-up schedule of 2021, completion of each event should correspond to the schedule in Figure 1. The schedule may shift depending on the NGNP reactor start-up schedule.

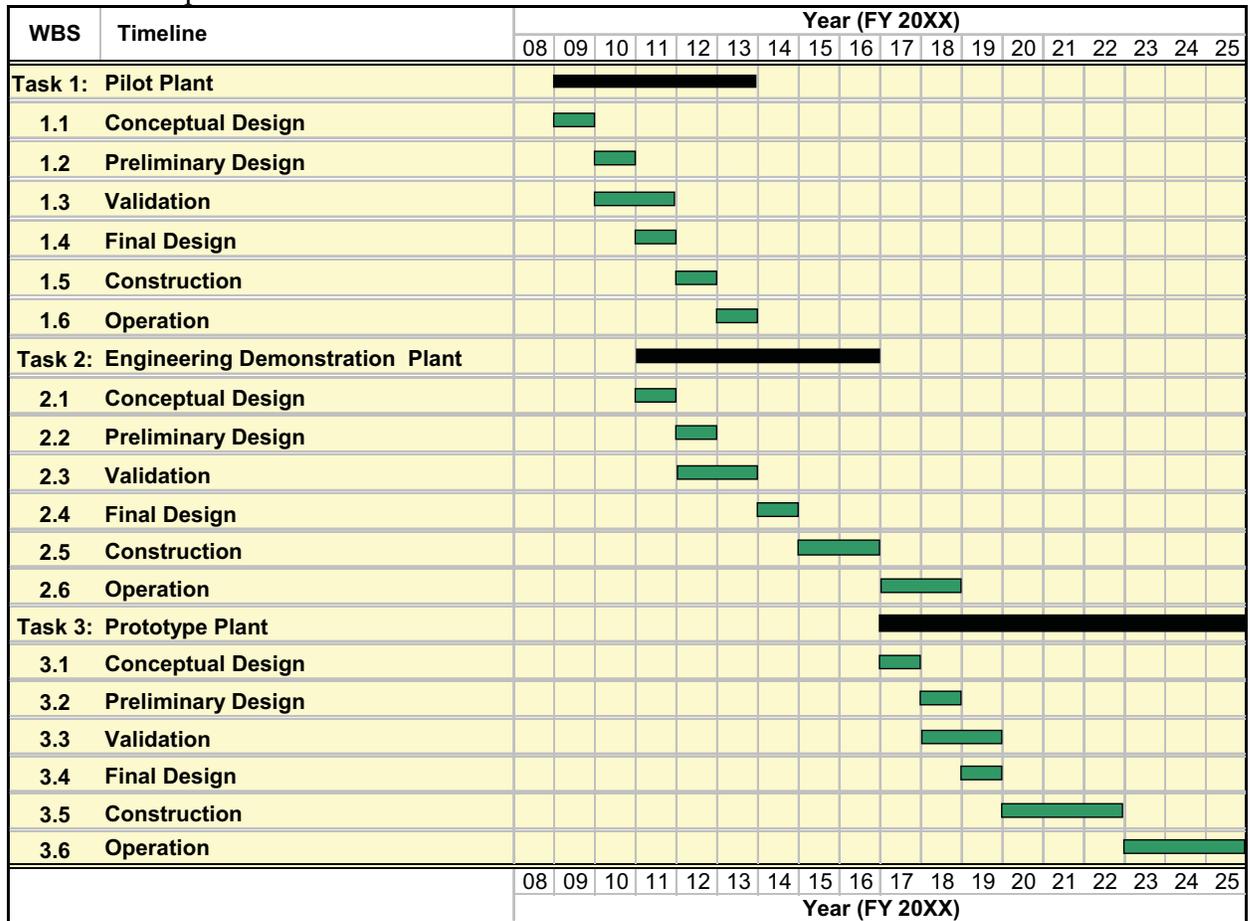| WBS	Timeline	08	09	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Task 1:	Pilot Plant	■	■	■	■	■	■												
1.1	Conceptual Design	▬																	
1.2	Preliminary Design		▬																
1.3	Validation			▬	▬														
1.4	Final Design				▬														
1.5	Construction					▬													
1.6	Operation						▬												
Task 2:	Engineering Demonstration Plant				■	■	■	■	■	■	■								
2.1	Conceptual Design				▬														
2.2	Preliminary Design					▬													
2.3	Validation					▬	▬												
2.4	Final Design							▬											
2.5	Construction							▬	▬										
2.6	Operation									▬	▬								
Task 3:	Prototype Plant									■	■	■	■	■	■	■	■	■	■
3.1	Conceptual Design									▬									
3.2	Preliminary Design										▬								
3.3	Validation											▬	▬						
3.4	Final Design											▬							
3.5	Construction															▬	▬		
3.6	Operation																	▬	▬

Figure 1. SI HPS Testing Schedule

The technology required to produce high-pressure hydrogen from a thermochemical plant coupled with nuclear power has not yet been demonstrated beyond laboratory scale. Development risks increase with plant capacity. Such risks should be mitigated by implementation of an early test program, developed to check feasible limits of operation.

Development Risk

The sulfur iodine process is currently at TRL 4+ level. The results of the ILS experiment at General Atomics, combined with the results of the Japanese glass system have validated the process chemistry and the majority of the components at relevant conditions. As the longest studied process, the task moving forward is almost exclusively one of engineering design and not fundamental science or invention. Even with this level of development and process maturity, there is still significant work to be done in order to demonstrate the process and reduce the development risk.

TRL 5 Requirements

TRL 5 requires lab scale integrated operation at relevant conditions. Only 3 tasks are remaining for the SI process to fully complete TRL 5. The first task involves the successful and reliable operations of the Bunsen reactor. The second task involves demonstrating reactive distillation. The third task involves the integrated operation of the entire process.

<u>Bunsen Reactor Operations</u>

The experiments performed at General Atomics on the ILS demonstrated the stand alone operation of all three process steps. Semi-integrated operations were routinely conducted with the sulfuric acid decomposition section and the Bunsen section. These operations involved the H_2SO_4 concentration and decomposition, SO_2 and O_2 production and the subsequent separation of the SO_2 and O_2. Additionally, the HI decomposition section was operated routinely, producing hydrogen at rates up to 75 l/hr. Semi-integrated runs between the Bunsen section and the HI decomposition section were also performed, where the lower phase material produced in the Bunsen reactor was processed through the HI decomposition skid after an off line air stripping to remove the sulfur components.

The major issue with these operations was the reliable operation of the Bunsen reactor. This challenge was a result of the engineering design of the system and an artifact of the scale of the process. With a target production rate of 100 l/hr H_2, the required process flows are on the order of 10s of ml/min. It was shown to be a challenge to design process equipment for these low flows while also attempting to operate the system at prototypical temperatures and pressures while constructed from engineering materials. The ability to pump and measure very small molten iodine flows was exacerbated by the difficulty in procuring industrial equipment at this scale. The result was a system with sporadic reliability. In retrospect, a target hydrogen production rate of 10-100 times larger would have facilitated the testing, allowing for standard, industrially available components to be utilized. It should be noted that when an appropriate industrial component was identified and implemented, that component performed as designed and without issues. These components included Badger meter valves, Lewa pumps and Rosemount differential pressure cells.

Reactive Distillation Demonstration

While extractive distillation was the process selected for the HI decomposition section of the ILS demonstration, subsequent analysis and recent data indicate that reactive distillation is the only viable path forward for sulfur iodine due to the high capital costs associated with the extractive distillation. Reactive distillation reduces the capital requirements of the process as well as leads to a higher overall efficiency. While the process has not been fully demonstrated at prototypical conditions, recent data supports the previous work done by General Atomics, indicating its viability for scale up.

Reactive distillation has two main zones, separation of the iodine from HI and water, and then a reaction zone. Both of these steps have been demonstrated separately. The issue which remains involves the catalyst longevity. Activated carbon is the preferred catalyst for the decomposition. The work remaining to be explored involves determining whether there is a deactivation of the catalyst over time as a result of iodine poisoning. The design relies on refluxed HI and water to wash the iodine off the catalyst. Investigations of the catalyst degradation would allow for design optimization to minimize these effects.

Integrated Operation

While semi-integrated operations were accomplished at the ILS at General Atomics, additional integrated tests are needed to fully validate the process engineering design and control as well as provide the data needed to design the next scale of demonstration. Successful operations of the Bunsen reactor and the reactive distillation process would provide the design data to validate the previously assumed and extrapolated data. This data can then be adjusted and fed back into the thermodynamic models, which allows for a higher confidence in scale up designs.

Materials Issues with the ILS

The experience gained in operating the three process sections in the ILS has refined the definition of the materials requirements for the S-I cycle. Early corrosion testing was necessary, but not sufficient to adequately specify materials for these service conditions. Although most materials selected for the ILS experiments functioned well, confirming the small sample corrosion testing, the potential for Ta vessel failures had to be addressed to support continued ILS testing. The implications of these materials problems for scaling to commercially relevant sizes also had to be addressed.

As a coating or liner on other substrate materials, Ta is acceptable, because the mechanical strength is provided by the substrate materials (such as stainless steel). Corrosion issues observed in some specialized components, such as valves, pumps, and compressors were anticipated because these were interim but expedient solutions implemented because there were limited options available for the small scale of the ILS.

Evaluation of the technology options existing at larger scales for the materials issues encountered in the ILS has led to the conclusion that most (not all) of the major

components used in the three primary S-I reaction sections can be based on existing commercial technologies. The commonly used glass or Teflon lined, or ceramic insulated vessel approaches developed in the chemical industry can generally be used at the larger scales for the lower temperature S-I applications. The exceptions are the areas where the temperature regime or configuration is different enough from commercial practice that additional testing and demonstration would be needed.

The Bunsen section operates at a relatively low temperature (120 °C), and therefore most components – including the primary reactor, can be fabricated using commercially available conventional glass or Teflon lined steels. Supporting piping, storage tanks related components are generally available at larges scale and in this temperature range. The primary application requiring additional testing is the demonstration of the heat removal capability in the Bunsen reactor. Examples of this heat exchange technology exist in industry, but needs to be demonstrated for the specific conditions of S-I.

The high temperature conditions for the decomposition of sulfuric acid were originally considered to pose the most significant materials challenges. The bayonet design adopted for the decomposer involves only SiC materials at high temperatures, and essentially eliminates corrosion concerns. The proposed decomposer scale up approach would be based on a multibayonet version of the ILS design. The multi-tube manifold for the bayonet decomposer would be fabricated as a Ta or Teflon coated/lined steel chamber. The approach is based on existing materials and designs but would require further design and demonstration at an intermediate scale (~10 tubes). Materials for the higher temperature seals (He side seals) for the decomposer/He interface also has to be demonstrated. Sulfuric acid concentration components required for the S-I cycle are available commercially.

Although the HI section materials encountered the most significant materials issues in the ILS, there are commercially available solutions for most HI section components when scaled to large sizes. Glass or Teflon lined steel components are suitable and available for the lower temperature piping and vessel components. For the higher temperature reactor vessels, Ta lined or ceramic insulated commercial technology vessels would be used. Materials and design approaches exist in commercial practice for these vessels (HI distillation and HI decomposition). For the largest scales, an additional alternative exists with ceramic insulated, lined steels. Heat input to the HI column can utilize commercial approaches. Process heat is provided to the system in the reboiler loop, rather than internal heat exchanger tubes.

Additionally, other materials not used in construction of the ILS should be evaluated. These include glass ceramics, a new glass coated steel capable of process temperatures up to 300ºC and internally insulated pipe. Insulated components with a corrosion resistant lining would allow the use of conventional engineering materials in higher temperature applications.

Conclusion

The sulfur iodine process is the most advanced and studied thermochemical process for nuclear hydrogen production. The process has been demonstrated in continuous operations in glass for up to a week, and in semi-integrated operations at relevant conditions utilizing engineering materials. As the only pure thermochemical process in consideration for demonstration on the NGNP plant, it is uniquely suited to efficiently utilize high temperature process heat. Sulfur iodine is also recognized internationally as the leading thermochemical process, with continued development in France, Japan, Korea, Italy and India.

The development work on the process to date has continued to validate the process capabilities. The process chemistry is confirmed, and the tasks remaining are engineering based. The data to date also gives a clear direction in what development areas need further exploration in order to reduce the risk and obtain the needed data for scale up designs. These area include development of reactive distillation for the HI decomposition, as well as a more thorough demonstration of the Bunsen reactor at relevant conditions. The sulfuric acid decomposition section design needs further optimization and the interface to the high temperature heat stream must be developed and validated.

All of these tasks are possible, relying only on continued engineering development. With over 30 years of work and investigation, no show-stopping issues have been identified, with the latest data supporting the possibility of increased efficiency and lower capital costs for the process. All of these factors lead to the conclusion that sulfur iodine is the best suited hydrogen process for demonstration with the NGNP.

Appendix A – Process Flowsheets and Stream Tables

Section 1 Flowsheet

Section 1 – The Bunsen Reaction

Streams	1	1a	3	4	30	31	32	40	50	41	51	33	34	10	11
Components	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec
SO2	89.11	89.11	87.44	1.67	87.44	87.44	87.44	52.46	34.98	52.46	34.98	87.44	87.44	0	0
H2O	22.49	22.49	0.84	21.65	0.84	0.84	0.84	0.50	0.34	0.50	0.34	0.84	0.84	22.13	366.37
O2	45.79	45.79	45.79	0.00	45.79	45.79	45.79	27.48	18.32	27.48	18.32	45.79	45.79	0	0
H2SO4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	91.61
I2	0	0	0	0	0	0	0	0	0	0	0	0	0	637.84	0
HI	0	0	0	0	0	0	0	0	0	0	0	0	0	1.80	0
g/sec	7578.6	7578.6	7081.7	496.8	7081.7	7081.7	7081.7	4249.0	2832.7	4249.0	2832.7	7081.7	7081.7	162519.0	15584.8
Phase	Vapor	Liq/Vap	Vapor	Liquid	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Liq/Vap	Liquid	Liquid
Temperature, C	90	25	24.999	24.999	95.218	61.483	128.75	128.75	128.75	76.939	76.939	76.94	25	130	130
Pressure, bar	5	5	5	5	10	10	19	19	19	19	19	19	19	50	130
Vapor Fraction	1	0.85184	1	0	1	1	1	1	1	1	1	1	0.42446	0	0

Streams	5	13	6	2	2a	2b	8	9	7	70	71	72	73	12
Components	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec
SO2	11.76	75.69	0.00	2.49	2.49	2.49	0	14.24	1.04E-05	1.04E-05	1.04E-05	1.04E-05	1.04E-05	0
H2O	0.00	0.84	247.67	187.80	187.80	187.80	893.80	435.42	1.20E-03	1.20E-03	1.20E-03	1.20E-03	1.20E-03	900
O2	45.15	0.64	0.00	0.00	0.00	0.00	0.00	0.13	0.99879	0.99879	0.99879	0.99879	0.99879	0
H2SO4	0	0	0	0	0	0	0	0	0	0	0	0	0	597.05
I2	0	0	0	0	0	0	0.61	0	0	0	0	0	0	205.91
HI	0	0	0	0	0	0	3.65	0	0	0	0	0	0	0.0
g/sec	2197.9	4883.9	4461.7	3542.6	3542.6	3542.6	16724.3	8760.5	-0.107	0.10161	0.044717	0.12924	-0.04944	-70.367
Phase	Vapor	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Vapor	Vapor	Vapor	Vapor	Vapor	Liquid
Temperature, C	25	25	25	90	25	25	100.11	24.14	25.051	104.67	4.0064	123.41	0.72982	130
Pressure, bar	19	19	19	90	25	25	50	19	19	19	5	5	1	3
Vapor Fraction	1	0	0	1	0	0	0	0	1	1	1	1	1	0

Section 1 – Stream Table

Section 2 – Sulfuric Acid Decomposition

Streams	6	15	36	37	38	39	43	44	45	46	47	48
Components	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec
H2SO4	0.02	91.61	91.59	91.59	6.91E-09	6.91E-09	127.28	127.28	127.28	9.73	0.13	0.13
H2O	247.66	366.37	118.71	118.71	210.30	210.30	67.15	67.15	67.15	184.69	194.30	194.30
SO2	0	0	0	0	91.59	91.59	0.16	0.16299	0.16299	0.16299	91.74	91.74
O2	0	0	0	0	45.80	45.80	8.34E-05	8.34E-05	8.34E-05	8.34E-05	45.80	45.80
SO3	0	0	0	0	5.14E-04	5.14E-04	2.89E-02	2.89E-02	2.89E-02	117.58	35.58	35.58
g/sec	4463.5	15584.8	11121.1	11121.1	11121.2	11121.2	13704.8	13704.8	13704.8	13704.8	13703.6	13703.6
Phase	Liquid	Liq/Vap	Liquid	Liquid	Vapor	Liq/Vap	Liquid	Liquid	Liq/Vap	Vapor	Vapor	Vapor
Temperature, C	25	80.05	219.98	219.98	138.7	90	305.42	305.42	403.31	600	850	375
Pressure, bar	0.2	0.1	1.5	5	5	5	5	6.6	6.6	6.6	5	5
Vapor Fraction	0	0.0839	0	0	1	0.4527	0	0	0.5411	1	1	1

Streams	16	17	18a	18b	19a	19b	20	22	23	24	25	26
Components	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec
H2SO4	91.61	0	82.45	82.45	9.16	9.16	9.16E-03	91.60	91.60	91.59	91.59	91.59
H2O	327.94	38.43259	295.14	295.14	32.79	32.79	170.75	157.18	157.18	130.27	130.27	130.27
SO2	0	0	0	0	0	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0	0	0	0	0	0
g/sec	14892.4	692.4	13403.1	13403.1	1489.2	1489.2	3077.0	11815.3	11815.3	11329.5	11329.5	11329.5
Phase	Liquid	Vapor	Liquid	Liq/Vap	Liquid	Liq/Vap	Vapor	Liquid	Liq/Vap	Liquid	Liquid	Liquid
Temperature, C	80.05	80.054	80.054	124.31	80.054	97.098	121	121	133.32	133.32	133.32	134.95
Pressure, bar	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	1.5	1.5
Vapor Fraction	0	1	0	0.4257	0	0.2261	1	0	0.1082	0	0	0

Section 2 – Stream Table (Continued Next Page)

Streams	49	52	42	11	53	54	27	28	29	31	35	56	57
Components	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec
H_2SO_4	0.13	0.44	92.00	91.61	1.93E-02	1.93E-02	91.59	2.53E-02	2.53E-02	1.01E-02	2.52E-02	6.70E-05	6.70E-05
H_2O	194.30	225.80	134.15	366.37	236.10	236.10	130.27	11.63	11.63	26.91	7.33E-02	11.56	11.56
SO_2	91.74	91.81	0.22	0	0	0	0	0	0	0	0	0	0
O_2	45.80	45.80	1.98E-04	0	0	0	0	0	0	0	0	0	0
SO_3	35.58	7.61E-04	2.72E-06	0	0	0	0	0	0	0	0	0	0
g/sec	13703.6	11457.7	11453.3	15584.8	4255.2	4255.2	11329.5	212.1	212.1	485.8	3.8	208.3	208.3
Phase	Vapor	Vapor	Liquid	Liquid	Liq/Vap	Liquid	Liq/Vap	Vapor	Liq/Vap	Vapor	Liquid	Liquid	Liquid
Temperature, C	222.52	240	238.78	130	116.03	25	220	220	165	133.32	165	90	90
Pressure, bar	5	5	5	3	0.1	0.1	1.5	1.5	1.5	0.1	1.5	1.5	1.5
Vapor Fraction	1	1	0	0	0.9999	0	0.0525	1	0.9915	1	0	0	0

Section 2 – Stream Table (Continued)

Section 3 Flowsheet

Hix from Sec 1

Iodine to Sec 1

Water to Sec 1

Water In

Power Generation

Heat Recovery

Hydrogen (120 bar)

P301, P302, E301, E302, E304, E305, E306, E307, E308, E309, E310, E311
C30, D30, SEP9, SEP10, T301

Streams: 8, 10, 12, 62, 64a, 64b, 65a, 65b, 66, 67, 68, 69, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96a, 96b, 97a, 97b, 98

Section 3 – Hydriodic Acid Decomposition

Streams	12	64a	64b	65a	65b	87	62	74	66	67	68	69	75	76	77
Components	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec
H2O	824.34	226.61	226.61	597.73	597.73	94.14	824.34	1174.69	1999.03	1998.93	22.13	22.13	2761.27	2761.27	2761.27
HI	188.60	51.85	51.85	136.76	136.76	8.51E-08	188.60	194.73	383.33	383.33	1.80	1.80	166.09	166.09	166.09
I2	546.86	150.33	150.33	396.53	396.53	0.007601	546.86	279.30	826.16	826.17	637.84	637.84	3.48	3.48	3.48
H2	0	0	0	0	0	0	0	0	0	0	0	0	91.58	91.58	91.58
g/sec	177773.0	48870.1	48870.1	128903.6	128903.6	1697.9	177773.0	116960.5	294733.6	294734.2	162519.0	162519.0	72057.9	72057.9	72057.9
Phase	Liquid	Liquid	Liq/Vap	Liquid	Liquid	Liquid	Liquid	Liquid	Liq/Vap	Liq/Vap	Liquid	Liquid	Vapor	Liq/Vap	Liq/Vap
Temperature,	130	131.6	309.99	131.6	260	22.299	131.6	296.56	293.91	313	374.8	160	286.04	272.24	270
Pressure, bar	3	50	50	50	50	50	50	50	50	50	50	50	50	50	50
Vapor Fraction	0	0	0.4008	0	0	0	0	0	0.0091	0.7329	0	0	1	0.3511	0.2971

Streams	78	79	80	81	82	83	84	85	86	8	10	89	92	93
Components	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec	mol/sec
H2O	1959.00	802.25	802.25	802.25	2.59	2.59	0.04	91.59	799.66	893.80	22.13	2240.19	506.58	506.58
HI	162.43	3.65	3.65	3.65	0	8.51E-08	0	0	3.650639	3.65	1.80	0	0	0
I2	2.87	0.61	0.61	0.61	7.60E-03	7.60E-03	1.28E-06	0	0.605332	0.61	637.84	0	0	0
H2	0	91.58	91.58	91.58	91.58	91.58	91.58	0	0	0	0	0	0	0
g/sec	56797.4	15259.7	15259.7	15259.7	233.2	233.2	185.4	1650.1	15026.4	16724.3	162519.0	40357.1	9126.1	9126.1
Phase	Liquid	Vapor	Liq/Vap	Liq/Vap	Vapor	Liq/Vap	Vapor	Liquid	Liquid	Liquid	Liquid	Vapor	Vapor	Vapor
Temperature,	270	270	241.12	108.32	108.32	25	22.299	20	108.32	100.11	130	368.31	260.02	94.19
Pressure, bar	50	50	50	50	50	50	50	50	50	50	50	102.7	2	0.3
Vapor Fraction	0	1	0.31301	0.10486	1	0.97309	1	0	0	0	0	1	1	1

Section 3 – Stream Table