Aspects of Hydrogen Production Using a SuperCritical Water-Cooled Nuclear Reactor

A. Lukomski[1], I. Pioro[1], K. Gabriel[2]
[1]Faculty of Energy Systems and Nuclear Science
[2]Faculty of Engineering and Applied Science
University of Ontario Institute of Technology
2000 Simcoe St. North, Oshawa, Ontario, L1H 7K4 Canada
E-mail: Andrew.Lukomski@uoit.ca, Igor.Pioro@uoit.ca, Kamiel.Gabriel@uoit.ca

Abstract

Thermochemical processes such as the copper chlorine (Cu-Cl) cycle decompose water to produce hydrogen as an alternative method to fossil fuel based production. An external energy source must be used to supply the high-temperature heat requirements of the cycle. Some Generation IV nuclear reactor design concepts operate at conditions which are sufficient to provide the necessary heat energy. Heat exchangers may provide an interface by which thermal energy is transferred from reactor coolant at 25 MPa and 625°C to a Cu-Cl based hydrogen-production facility. Characteristics of a connection between a nuclear power plant and a hydrogen production facility are discussed.

1. Introduction

Hydrogen is not readily available in significant quantities and thus is categorized as a secondary energy carrier. It must be produced from a primary energy source such as fossil fuels, renewable energy (biomass, hydro, solar, etc.), or nuclear power. The majority of the hydrogen produced in the United States, accounting for approximately 20% (9-10 Mt/year) of the world's total supply, comes from steam reforming of natural gas [1]. Fossil fuels continue to be the most economical energy source for hydrogen production mainly due to the high costs associated with renewable technologies.

Typical applications of hydrogen have been limited mainly to the petrochemical, automotive and food industries. Within the petrochemical industry, production and consumption frequently occurs on the same site limiting the distribution network of hydrogen. Larger scale integration of hydrogen into the commercial sector would depend heavily on reliable production and storage technologies which are currently being researched. Centralized hydrogen production would be suitable to a fossil fuel or nuclear fuel based energy source while small scale hydrogen facilities could be coupled with renewable technologies. Estimated costs for large scale facilities range between US$2.0-2.2/kg H_2 with corresponding small and mid-sized scale plants at levels 3 times as high [1].

The advancement of hydrogen technology has been supported globally by initiatives such as the Hydrogen Implementing Agreement (HIA), a program established by International Energy Agency (IEA) members in 1977. Thermochemical cycles were investigated extensively during the same time frame identifying select high efficiency cycles. Due to the high costs associated with commercial development at the time further research was abandoned [2]. Interest in thermochemical cycles has recently been revived due in part to the global movement to reduce dependence on greenhouse gas emitting fuel sources.

2. Hydrogen production via thermochemical cycles

Thermochemical decomposition of water is an attractive method of hydrogen production where cyclic processes recycle intermediate reaction materials in a closed loop. The sole system inputs are water, thermal energy and electrical energy. Over 200 thermochemical cycles have been identified as potential processes to generate hydrogen [3], many relying on heat from external sources such as solar power [4]. Extreme high temperature requirements, low process efficiencies and unfavourable reaction kinetics, however, have limited further development of many of the cycles considered. Pursuant to the US Department of Energy's Nuclear Hydrogen Initiative (NHI), a research team at Argonne National Laboratory (ANL) along with several other universities, narrowed focus down to 9 cycles characterized by reasonable process temperatures, efficiencies and completion of proof-of-principle experiments [4]; the cycles are: cerium-chlorine (Ce-Cl), calcium-bromine (Ca-Br), iron-chlorine (Fe-Cl), magnesium-iodine (Mg-I), vanadium-chlorine (V-Cl), copper-chlorine (Cu-Cl), copper sulphate (Cu-SO_4), potassium bismuth (K-Bi), and hybrid chlorine [5].

Another promising cycle is the Sulphur-Iodine (SI) process which involves the decomposition of sulphuric acid at temperatures exceeding 800°C followed by processing of intermediate materials and decomposition of hydrogen iodide at 300°C to form hydrogen gas. Select Generation IV nuclear reactors, specifically Gas Cooled Fast Reactors (GCFR) like the modular heat reactor with a coolant outlet temperature of 850°C can supply the needs of the cycle. Richards et al. [6] developed conceptual designs to link a modular helium GCFR to a SI based hydrogen production facility. It is argued that the design of the neighbouring facilities should place them as close as possible, approximately 100 m apart, to minimize heat loss from the high-temperature coolant. Experimental efficiencies for the SI cycle have been measured up to 50% [7].

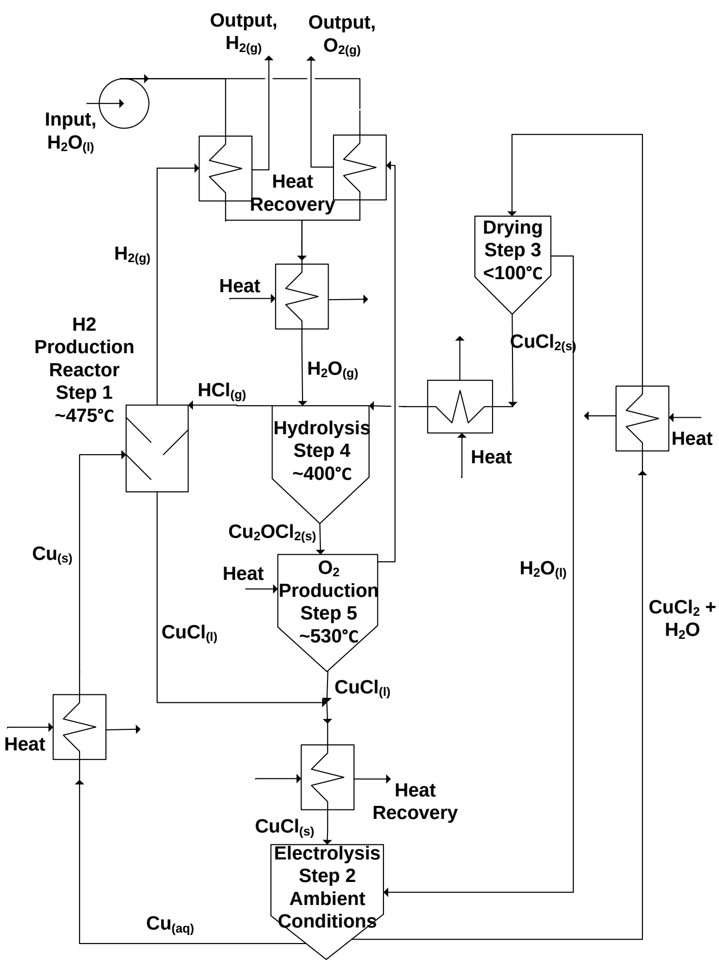
A major limitation of many thermochemical cycles are the high temperatures required for certain process steps. This is not representative of the Cu-Cl cycle which has a relatively low temperature requirement. Given the ~530°C that is required for endothermic decomposition of an intermediary reactant, a SuperCritical Water-cooled Nuclear Reactor (SCWR) having a coolant temperature at the reactor outlet of 625°C is a potential energy source that can be applied to a Cu-Cl based hydrogen production facility.

2.1 Copper chloride cycle characteristics

Of the 9 cycles identified by the NHI assessment, the Cu-Cl cycle was selected as most promising for ongoing development and Atomic Energy of Canada Ltd. (AECL), selected it as the optimal cycle for thermochemical hydrogen production with a SCWR [8]. Rationale for this includes high product yields, reactions which progress into completion without side reactions, potential for heat recycling within the cycle, and relatively high cycle efficiencies [3], [9]. Furthermore, the lower temperature requirements reduce stresses on materials of construction. Researchers at the University of Ontario Institute of Technology (UOIT) in collaboration with

ANL and AECL have been advancing Cu-Cl cycle technology through the international Nuclear Energy Research Initiative [8].

Hybridization of the Cu-Cl cycle enables the combination of reaction steps to simplify the process. The 5 step cycle requires the handling of solid copper particles which react with hydrogen chloride gas in the hydrogen production step at temperatures of ~475°C. A schematic of this variation along with the intermediate reactants/products is shown in Figure 1. The drying method of cupric chloride, set as Step 3, can have a significant impact on the overall heat requirements of the cycle. Where $CuCl_2$ is dried as a slurry mixture, the overall heat demand for the cycle accounting for endothermic reactions, drying and heating is 277.4 kJ/g of H_2 produced; a direct (spray) drying of the solution would increase this to 681.9 kJ/g of H_2 [3]. Exothermic reactions, cooling and solidification processes release 116 kJ/g H_2 which can be recycled to supply endothermic reactions or pre-heat reactants.



Step	Feed	Output
1	Electrolytic Cu, dry HCl, *Q*	H_2, $CuCl_{(l)}$ salt
2	Granular CuCl, HCl, *V*	Electrolytic Cu, HCl and $CuCl_2$ slurry
3	HCl and $CuCl_2$ slurry, *Q*	Granular $CuCl_2$, H_2O/HCl vapours
4	Granular $CuCl_2$, H_2O	Granular $CuO*CuCl_2$, 2HCl
5	Granular $CuO*CuCl_2$, *Q*	Molten CuCl salt, O_2
Q, thermal energy; *V*, electrical energy Alternate 4-Step Cycle (combine steps 1-2) $2CuCl_{(aq)} + HCl_{(aq)} \rightarrow H_{2(g)} + 2CuCl_{2(aq)}$		

Figure 1. Conceptual schematic and reaction materials of the 5-step Cu-Cl cycle [3].

Fully recycling the heat energy produced from exothermic reaction steps would significantly reduce the demand of external energy required for the cycle. Assuming no heat loss to the environment the efficiency of the Cu-Cl cycle is 46% without heat recycling implemented. If 100% of the available heat energy were to be recycled the efficiency would increase to 74% [3].

Recycling all heat energy within the cycle is not achievable as heat losses through piping must be accounted for. Moreover, a portion of the heat produced within the cycle is in the form of low-temperature water or powder which could prove to be uneconomical in full scale applications [10].

3. External process heat source

Several technologies are capable of supplying the process heat requirement for the Cu-Cl cycle including SCWR design concepts, other Generation IV nuclear reactors and solar powered facilities. Nuclear reactors provide a constant and reliable thermal power source which makes them ideal for process heating applications in addition to baseload power generation. Daily variations in power demand lead to excess electrical energy which could have been delivered to a hydrogen production facility as high temperature coolant. A high temperature Heat Exchanger (HE) is used as the interface between the two facilities where the reactor coolant transfers heat to water or a process fluid flowing directly through the thermochemical facility or to an intermediate loop.

As part of the NHI research is underway in various topic areas to support linking of a SI cycle facility to a high temperature GCFR. The design focuses on the development of an intermediate heat transport loop to transfer high temperature thermal energy from the reactor to the hydrogen production facility [11]. Materials research into high temperature alloys, ceramics, and refractory metals is ongoing with modeling of two-HE system designs at several facilities within the United States. Initial safety assessments based on statistical and risk-based analysis suggest that configuration of the facilities may be a distance of 60-110 m apart [11].

A conceptual layout developed by Ferrandon et al. [12] for a three step hybrid (some literature do not categorize drying as an official reaction) Cu-Cl cycle facility provided an interface with the external source at two points within the system loop: the steam generator prior to the hydrolysis and the oxygen production (copper oxychloride decomposition) reactors. Similarly, the five step variation would require the majority of external heat to be delivered to those locations in addition to the $CuCl_2$ drying equipment.

3.1 SCWR cogeneration layouts

Various conceptual designs for SCWR Nuclear Power Plants (NPPs) have been assessed using heat and mass balance analysis. The SCWR-hydrogen production facility could potentially be integrated with several SCWR NPP layouts including no-reheat or single reheat cycles with and without heat regeneration. Naidin et al. [13] suggested a single re-heat regenerative cycle layout as the basis for a SCWR NPP cogeneration facility due to higher efficiency operation compared to no re-heat options investigated. The advantage of the increased efficiency is countered by increased complexity of the system which will require additional design development. Due to the potential hazards of NPP operation any HEs interfacing with the highly pressurized reactor coolant would need to be located inside of the NPP’s containment structure.

3.1.1 No re-heat NPP layout

For a no-reheat regenerative NPP layout three extraction points used for a HE to connect the NPP with a hydrogen production facility were outlined by Naidin et al. [14]: reactor outlet, High Pressure (HP) turbine outlet, HP turbine extraction steam outlet. Figure 2 shows a schematic of a possible no-reheat cycle along with coolant parameters. Lukomski et al. [15] concluded that due to the low mass flow rate a HE located at the HP turbine's steam extraction point would not be capable of supplying the amount of process heat required for full scale hydrogen production. This assumes that there is no heat recycling within the Cu-Cl facility. A HE located at the reactor outlet could be developed as a double tube, recuperative type designed for supercritical water conditions on the reactor loop side and superheated steam conditions on the hydrogen facility side. If an intermediate process loop is not incorporated into the design the pressure on the SCWR side may be up to 250 times larger than that on the hydrogen production loop. The second potential location on the reactor side loop would be immediately after the HP turbine exit where the coolant exists as superheated steam. Materials in the intermediate loop would not be in an environment as harsh as the primary loop.

For the no-reheat cycle layout the minimum amount of thermal power required from the reactor would be 11.9% as shown in Table 1 for several heat loss scenarios. It is likely that heat losses will be significant given the distance between the two facilities may be approximately 100-150 m. Thus, the amount of internal heat recycling designed into the Cu-Cl cycle hydrogen production facility may be driven by the proximity of the two production loops. Variation in coolant enthalpy as well as the difference in available coolant to be diverted between the two locations is responsible for the different mass flow rates required through the HEs.

Table 1. SCWR NPP - No re-heat layout heat exchanger parameters to supply process heat for a hydrogen production facility operating at H_2 production of 1 kg/s

	Cu-Cl Cycle System Heat Losses %				
	0	10	20	30	40
Total P_{th} Required, %	11.9	13.2	14.8	17.0	19.8
Reactor Outlet Heat Exchanger NPP Mass Flow (kg/s)	142.6	158.5	178.3	203.7	237.7
HP Turbine Outlet Heat Exchanger NPP Mass Flow (kg/s)	151.4	168.3	189.3	216.4	252.4

3.1.2 Single re-heat NPP layout

A single re-heat NPP cycle was proposed by Naidin et al. [15] which involved two potential HE locations: reactor outlet and re-heater outlet. Figure 3 shows a schematic of the possible single re-heat cycle along with coolant parameters. Similar to the no re-heat layout, a HE located at the reactor outlet would be designed for a supercritical water / superheated steam interface. The addition of re-heater channels introduces an additional high temperature extraction point at a much lower operating pressure. Table 2 shows the process parameters for both HEs considered. Calculated mass flow rates required through the post re-heat channels HE is lower compared to the reactor outlet layout due to higher fluid enthalpy conditions. Although lower mass flow rates are expected for the single re-heat layout there is a slight drop in the efficiency for this arrangement.

Table 2. SCWR NPP - Single re-heat layout heat exchanger parameters to supply process heat for a hydrogen-production facility operating at H_2 production of 1 kg/s

	Cu-Cl Cycle System Heat Losses %				
	0	**10**	**20**	**30**	**40**
Total P_{th} Required, %	12.0	13.3	15.0	17.1	20.0
Reactor Outlet Heat Exchanger Mass Flow (kg/s)	142.5	158.4	178.2	203.6	237.6
Reheater Outlet Heat Exchanger Mass Flow (kg/s)	114.9	127.6	143.6	164.1	191.5

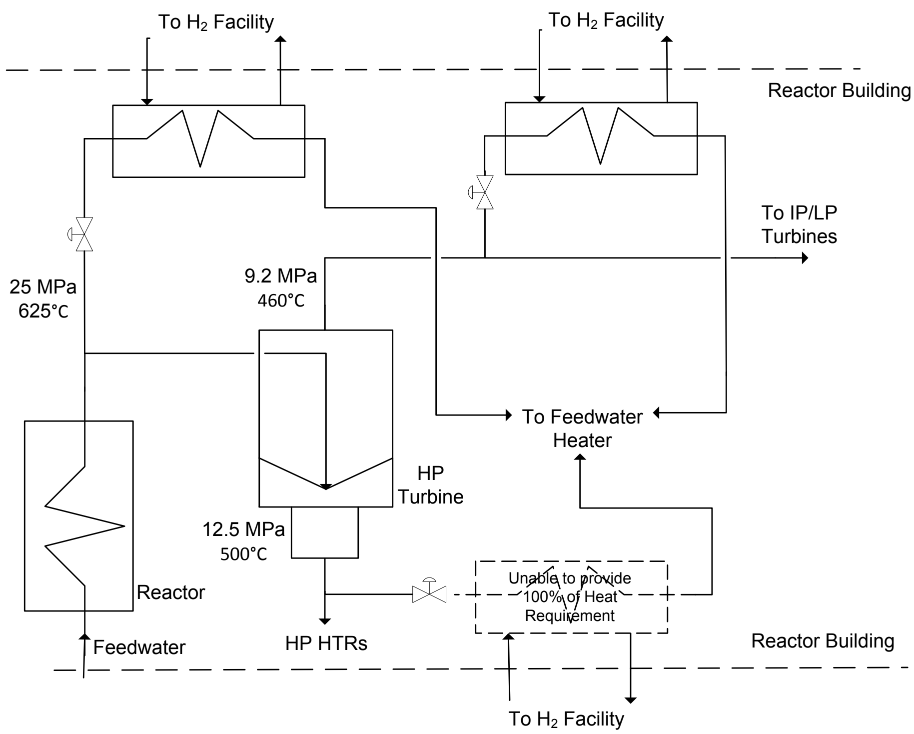


Figure 2. Candidate inter-facility heat exchanger locations for a proposed no-reheat SCWR NPP [14].

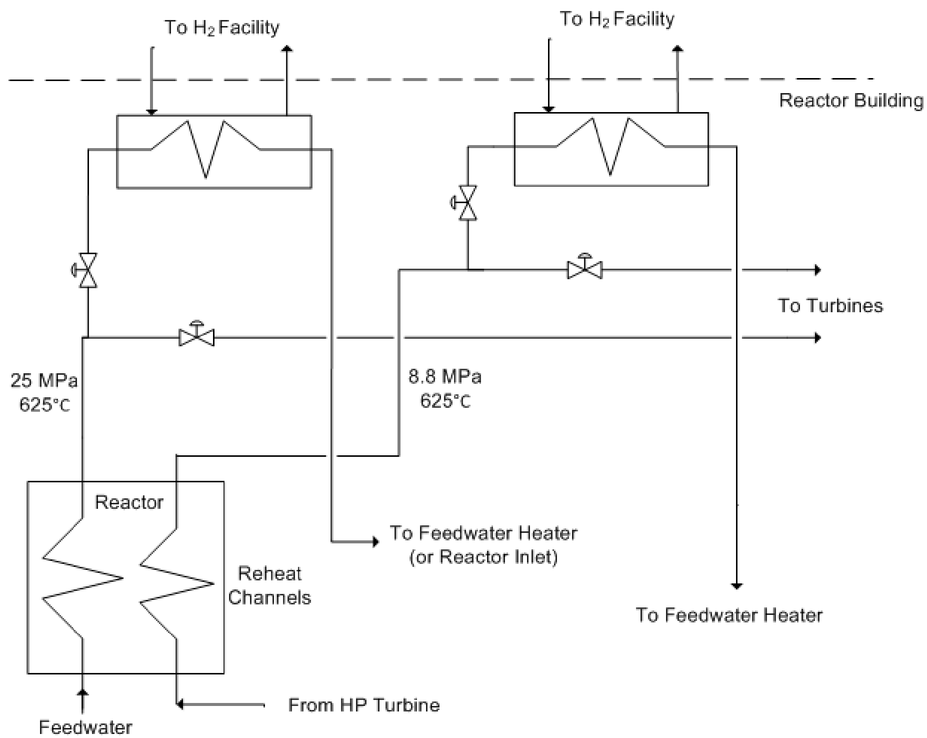


Figure 3. Candidate inter-facility heat exchanger locations for a proposed single-reheat SCWR NPP [14].

3. 2 Impact on the electrical grid

Supplying process heat to a Cu-Cl cycle based hydrogen production facility would be the secondary objective for a SCWR. The design of the inter-facility HE must incorporate control mechanisms to minimize undesirable transients in the reactor loop resulting from events occurring in the hydrogen facility. The SCWR power output is independent of process heating requirements and can be maintained at a constant level with electrical output scaled down during times of increased hydrogen production and vice versa during periods of higher electrical demand. Due to the nature of reactor design, NPPs are not suitable for load following and thus are effective in providing reliable, low-cost, baseload electricity. During off-peak generating hours an NPP could provide 100% of the heat energy required by the hydrogen production facility with reduced electrical output as a consequence. A more suitable load following generating resource such as hydroelectric could be used to deliver the difference in electrical output.

Analysis conducted by Naidin et al. [14] for potential no-reheat and single reheat SCWR NPP cycles identified efficiencies of approximately 50% and 51%, respectively, for a 1200 MW_{el} rated plant. Lukomski et al. [15] determined that a SCWR in a no re-heat layout and HE at the reactor outlet supplying the full heat requirements to a Cu-Cl facility as well as the electrical energy requirements of 31.3 kJ/g of H_2 produced would reduce electrical output to 1004 MW_{el}, approximately a 16% drop. Further analysis for a single re-heat layout with a HE in the same location would drop electrical output to 976 MW_{el}, approximately a 19% drop. These results assume no net heat loss from the Cu-Cl cycle, requiring that a minimum fraction of internal heat would need to be recycled to obtain the conditions shown above. The same percentage drop in power transferred to the turbine shaft is assumed in the preceding analysis. The utilization factors for the no-reheat and single reheat layouts with negligible system heat losses are approximately 55% and 54%, respectively. For a HE located immediately after the reactor outlet, the no re-heat cycle proposed by Naidin et al. [14] would be more effective as a cogeneration facility compared to the single re-heat layout.

4. Conclusion

Hydrogen production using the thermochemical copper chlorine cycle may be supported through process heat supplied by a SCWR. The current SCWR concept has reactor outlet conditions reaching 25 MPa and 625°C which exceed the highest temperature requirements for reaction steps in the Cu-Cl cycle. Development of a link between a NPP and hydrogen production facility can be accomplished via a HE. This connection support non-carbon based hydrogen production while increasing the overall utilization factor for the NPP. Conclusions that can be drawn from the above discussion are:

1. The copper chlorine cycle has been identified by the NHI as the most promising thermochemical cycle for further commercial development; AECL selected the Cu-Cl cycle as the most suitable to be linked with a SCWR NPP
2. Potential layouts for a link between a SCWR NPP and Cu-Cl cycle based hydrogen production facility linking HE may be designed for the no-reheat and single reheat reactor loops;
    - i) the no-reheat cycle layout may involve a HE at the reactor outlet, the HP turbine outlet or the HP turbine extraction point outlet, provided supplemental heating is available
    - ii) the single reheat cycle layout may involve a HE at the reactor outlet or the reheater outlet
3. A no re-heat layout HE located at the reactor outlet or HP turbine outlet would meet the heat requirements of the hydrogen production facility while minimizing the thermal energy diverted from the NPP: for the ideal case, as little as 11.9% of the SCWR NPP's thermal power for a 1 kg/s production rate of H_2 gas would be required.
4. Process heating impact on the electrical output from the SCWR NPP is dependent on the cycle layout selected and the position of the HE. A HE located at the reactor outlet in a no re-heat cycle will produce a smaller drop in electrical output of the SCWR NPP compared to a single re-heat cycle of the same layout. Based on the analysis above, the highest utilization factor is for the no re-heat cycle.

5. Acknowledgements

Financial supports from the NSERC/NRCan/AECL Generation IV Energy Technologies Program and NSERC Discovery Grant are gratefully acknowledged.

6. Nomenclature

Q Thermal Energy
V Electrical Energy
P_{th} Thermal Power

7. References

[1] Rand, D.A.J and Dell, R.M. "Hydrogen energy – challenges and prospects", The Royal Society of Chemistry: Cambridge, UK, 2008.

[2] International Energy Agency. "Hydrogen production and storage – R&D priorities and gaps", IEA – Hydrogen Co-Ordination Group, 2006.

[3] Naterer, G.F, Gabriel, K., Wang Z.L., Daggupati V.N., Gravelsins R. "Thermochemical hydrogen production with a copper-chlorine cycle. I: Oxygen release from copper oxychloride decomposition", International Journal of Hydrogen Energy. Vol. 33, Iss. 20, 2008, pp. 5439-5450.

[4] Lewis, M, and Taylor, A. "High temperature thermochemical processes", DOE Hydrogen Program, Annual Progress Report, Washington, DC; 2006, pp. 182-185.

[5] Lewis, M.A., Masin, J.G. "The evaluation of alternative thermochemical cycles – Part II: The down-selection process", International Journal of Hydrogen Energy, Vol. 34, Iss. 9, 2009, pp. 4125-4135.

[6] Richards, M., Shenoy, A., Schultz, K., Brown, L., Harvego, E., McKellar, M., Coupey, J.P., Reza, S.M.M., Okamoto, F., Handa, N., "H2-MHR conceptual designs based on the sulphur-iodine process and high-temperature electrolysis", International Journal of Nuclear Hydrogen Production and Applications Vol. 1, No. 1, 2006, pp. 36-50.

[7] Jones, R. H., "Materials for the hydrogen economy", CRC Press. Taylor & Francis Group: Boca Raton, Florida, 2008.

[8] Naterer, G. F., Gabriel, K., Lu, L., Wang, Z., Zhang, Y. "Recent advances in nuclear based hydrogen production with the thermochemical copper-chlorine cycle", Journal of Engineering for Gas Turbines and Power, Vol. 131, 2009, pp. 032905-1-10.

[9] Naterer, G., Suppiah, S., Lewis, M., Gabriel, K., Dincer, I., Rosen, M.A., Fowler, M., Rizvi, G., Easton, E.B., Ikeda, B.M., Kaye, M.H., Lu, L., Pioro, I., Spekkens, P., Tremaine, P., Mostaghimi, J., Avsec, J., Jiang, J., "Recent Canadian advances in nuclear-based hydrogen production and the thermochemical Cu-Cl cycle", International Journal of Hydrogen Energy. Vol. 34, 2009, 2901-2917.

[10] Wang, Z., Gabriel, K., Naterer, G.F. "Thermochemical process heat requirements of the copper-chlorine cycle for nuclear-based hydrogen production", Proceedings of the 29th Conference of the Canadian Nuclear Society, Toronto, Ontario, Canada, 2008 June 1-4.

[11] Sherman, S. R. "Nuclear reactor/hydrogen process interface", DOE Hydrogen Program, Annual Progress Report, Washington, DC; 2006. Pp. 186-189.

[12] Ferrandon, M.S., Lewis, M.A., Tatterson, D.F., Nankani, R.V, Kumar, M., Wedgewood, L.E, Nitsche, L.C. "The hybrid Cu-Cl thermochemical cycle. I. conceptual process design and H2A cost analysis. II. limiting the formation of CuCl during hydrolysis", extended Abstract submitted for the NHA Annual Hydrogen Conference 2008, Sacramento, CA, United States of America, 2008 March 31-April 4.

[13] Naidin, M., Mokry, S., Baig, F., Gospodinov, Y., Zirn, U., Pioro, I., Naterer, G. "Thermal design options for pressure-channel SCWRs with cogeneration of hydrogen", Journal of Engineering for Gas Turbines and Power, Vol. 131, 2009, pp. 012901-1-8.

[14] Naidin, M., Mokry, S., Monichan, R., Chopla, K., Pioro, I., Naterer, G., Gabriel, K. "Thermodynamic analysis of SCW NPP cycles with thermo-chemical co-generation of hydrogen", Proceedings of the International Conference on Hydrogen Production, Oshawa, Ontario, Canada, 2009 May 3-6.

[15] Lukomski, A. J., Pioro, I., Gabriel, K. "Aspects of Hydrogen Co-Generation Using a Thermochemical Cycle Linked to a SuperCritical Water-cooled Nuclear Reactor", Proceedings of the 2nd Canada-China Joint Workshop on Supercritical Water-Cooled Reactors, Toronto, Ontario, Canada, 2010 April 23-28, 2010.