*2021 International Nuclear Atlantic Conference – INAC 2021*
*Virtual meeting, Brazil, November 29 – December 2, 2021*

ISBN: 978-65-594-1256-3

# Comparison between two thermochemical hydrogen production methods and seawater desalination coupled to the HTR-PM nuclear reactor

Daniel González Rodríguez[1], Fernando Roberto de Andrade Lima[1,2] and Carlos Alberto Brayner de Oliveira Lira[1,2]

[1]*danielgonro@gmail.com, Centro Regional de Ciencias Nucleares do Nordeste, Avenida Professor Luiz Freire, nº 200, Cidade Universitária, Recife - PE | CEP: 50.740-545*
[2] *Universidade Federal de Pernambuco, Departamento de Energia Nuclear, Av. Prof. Moraes Rego, 1235 - Cidade Universitária, Recife - PE - CEP: 50670-901.*

## 1. Introduction

Hydrogen economy is one of the most innovative energy concepts since the big oil time in the '20s. It proposes the substitution of fossils fuels as the baseline of the global energy system for another energy carrier, hydrogen. Since the emergence of the concept of hydrogen economy its production was identified as the main aspect to improve. Generation IV nuclear reactors have been studied in recent years by various research groups. Hydrogen production with competitive efficiency values is one of the main remaining challenges of the hydrogen economy concept. Due to this, the majority of the studies carried out on this subject are directed to the determination of the efficiency of the hydrogen production process using an advanced nuclear reactor.
The sulfur-iodine cycle was determined to be the best cycle for coupling to the helium nuclear reactor because of its high efficiency and potential for further improvement. The SI process has also successfully completed bench-scale demonstrations at atmospheric pressure. The HTR-PM project arises from the results of reactor HTR-10 in early November 2005. Plant operating lifetime is envisaged as 40 years with an 85% load factor. The capital cost per kW is expected to be 75% of the small HTR-PM, and for subsequent units, 50% [1].
Due to the advantages of this type of technology, this project has always been linked to the possible cogeneration of electricity and hydrogen to take advantage of the maximum capacities that the high temperatures provide. Given the technological advantages of the HTR-PM project and its operating parameters, its evaluation as a primary source of energy to produce hydrogen is interesting. In this case, two hydrogen production processes will be evaluated by thermochemical cycles: SI cycle and Cu-Cl cycle. Both processes will be in cogeneration to desalinate seawater through an Multi Stage Flash system.
The SI process is composed of three chemical reactions resumed in Table 2. The SI cycle is a closed process, all the chemical components are recycled at a theoretical yield of 100%. Theoretically, only water, as the raw material for the process, must be incorporated continuously.

Table 2 – Chemical reactions of the SI cycle.

| Section | Reaction | $\Delta H^0(kJ/mol)$ |
|---|---|---|
| Bunsen | $SO_2(g)+(1+x)I_2(l)+(2m+n)H_2O \rightarrow H_2SO_4 mH_2O(aq)+2HI+xI_2+nH_2O(l)$ | -126 |
| H2SO4 | $H_2SO_4(g) \rightarrow H_2O(g)+SO_3(g)$ | 97.54 |
| | $SO_3(g) \rightarrow SO_2(g)+\frac{1}{2}O_2(g)$ | 98.92 |
| HI | $2HI(g) \rightarrow I_2(g)+H_2(g)$ | 119 |

Another production method planned for the concept of a hydrogen economy is the use of thermochemical water dissociation cycles. There are more than 70 known cycles, but only about 5 are being studied with greater interest from recent years [2]. Within these the Copper-Chlorine (Cu-Cl) cycle covers a large part of the efforts of the main research groups worldwide. There are 3 variants of this process, differing mainly in the number of chemical reactions involved in the cycle. The 4-step variant is defined by the following chemical reactions:

$$2CuCl\left(aq\right)+2HCl\left(aq\right)\overset{25\,^{\circ}C}{\rightarrow}H_2\left(g\right)+2CuCl_2\left(aq\right) \qquad \text{Electrolysis reaction (1)}$$

$$Cu_2OCl_2\left(s\right)\overset{500\,^{\circ}C}{\rightarrow}\frac{1}{2}O_2\left(g\right)+2CuCl\left(l\right) \qquad \text{Thermolysis reaction (2)}$$

$$2CuCl_2\left(s\right)+H_2O\left(aq\right)\overset{400^{\circ}C}{\rightarrow}Cu_2OCl_2\left(s\right)+2HCl\left(g\right) \qquad \text{Hydrolysis reaction (3)}$$

$$CuCl_2\left(aq\right)\overset{80^{\circ}C}{\rightarrow}CuCl_2\left(s\right) \qquad \text{Drying step (4)}$$

This process is considered as hybrid when presenting an electrolysis reaction, for which it requires the supply of a certain amount of electrical energy. The main advantage of this process is that although the necessary temperatures are high (~ 500 $^{o}$C) are lower than those necessary for other thermochemical processes such as the SI (Sulphur-Iodine).

The seawater desalination method proposed will be the MSF due to the low energy requirements that make it ideal for cogeneration systems taking advantage of residual heat. This method is based on flash evaporation. In this, the seawater is evaporated reducing the pressure in opposition to the increase in temperature. The heat of condensation released in each stage increases the temperature of the incoming water in the next. These plants consist of a heat input and several distillation sections where it is released

## 2. Methodology

For the study of the proposed systems for the SI and Cu-Cl process, the Rankine cycle for the power generation will be analyzed initially. Once calculated, it will be used for both hydrogen production processes. The conceptual designs are developed in computational models in Aspen Plus® to calculate the efficiency of the main component cycle. The Rankine cycle, Cu-Cl process, and the SI process will be analyzed separately before the complete systems. Some model operating parameters can be estimated for a fixed operating power of the HTR-PM dedicated to the hydrogen production processes.

The chemical process simulation program is commonly used in similar works and published by the most recognized research groups on the subject. It has a broad base of chemical components that can be used, as well as mathematical models applicable to complex problems such as thermochemical cycles. For the construction of the flowcharts of the proposed systems the following considerations were adopted:

- The simulation was performed in steady-state and operating with the nominal parameters.
- The influence of gravity and kinetic energy on the components is neglected.
- Heat losses in components, pipes, and joints are neglected.
- Pressure drops in the pipes are also neglected.

These assumptions do not compromise the quality of the results since they are typical assumptions in conceptual project analyzes. In this case, two types of thermodynamic properties packages are used for the mathematical description of the system. The Peng-Robinson model is mainly used for the state equation for gases involved in the Rankine cycle, SI and the Cu-Cl processes [3]. For the description of the chemical reactions involved in the SI and Cu-Cl processes, the NRTL (Non-Random Two Liquids) and “Solids” models were selected for the management of the solid’s compounds present in the Cu-Cl process.

In order to calculate the overall efficiency of the proposed system, the mass, energy, and exergy balances are performed using the following expressions:

$$\sum \dot{m}_{in} - \sum \dot{m}_{out} = 0 \tag{5}$$

$$\dot{Q}_{in} - \dot{Q}_{out} + \dot{W}_{in} - \dot{W}_{out} = \sum_{out} \dot{m}\left(h_{PT} - h_0 + h_f\right) - \sum_{in} \dot{m}\left(h_{PT} - h_0 + h_f\right) \tag{6}$$

$$\dot{Ex}_{\dot{Q}_{in}} - \dot{Ex}_{\dot{Q}_{out}} + \dot{Ex}_{\dot{W}_{in}} - \dot{Ex}_{\dot{W}_{out}} = \sum_{out} \dot{m}_{out} ex_{out} - \sum_{in} \dot{m}_{in} ex_{in} + \dot{Ex}_d \tag{7}$$

## 3. Results and Discussion

In this work, two novel conceptual designs for hydrogen production processes coupled to a novel Rankine cycle using the 2x250 MWth version of the HTR-PM project were analyzed. Two processes were considered for the hydrogen production, the high temperature electrolysis process, and the Cu-Cl cycle. A new proposal for cogeneration of hydrogen and seawater desalination is developed for the 2x250 MWth project of the HTR-PM reactor. Using a computational model, the efficiency of the Rankine cycle is calculated as well as the exergy efficiency of the main components of the cycle. The value obtained for the energy efficiency of the Rankine cycle is in the range reported by other authors [4].

$$\eta_{Rankine} = \frac{\dot{W}_{turbine} - \dot{W}_{pump}}{\dot{Q}_{HTR-PM}} = 38.55\ \% \tag{8}$$

A computational model was built in a chemical process simulator to optimize some operating parameters for the conceptual design for the Cu-Cl cycle coupled to the 2x250 MWth HTR-PM through the analyzed Rankine cycle.

This computational model allows us to carry out several parametric studies, optimizing some of them for the HTR-PM. Using this computational model, we determined the amount of water that can be processed by the Cu-Cl cycle as well as the amount of $CuCl_2$ corresponding to it. These values had a marked influence on the efficiency of the section because of the energy consumption in several components, especially the dryer.

With this analysis, we can determine the less efficient components of the section, as well as those with greater energy needs. In this case, the chemical reactor present values in the range of other similar studies, showing the lowest efficiency values in B24, corresponding to the oxy-decomposition reaction. This component also has the highest energy destruction rates for all chemical reactors because it is the component with the highest temperature.

$$\eta_{Cu-Cl} = \frac{m_{H_2} \Delta LHV_{H_2}}{W_E + Q_{B7} + Q_{B24} + Q_{B28} + Q_{DRYER} + \left(m_{s4} h_{s4} - m_{s5} h_{s5}\right)} = 32.12\% \tag{9}$$

The proposed model allows the complete and closed connection of the SI cycle and the HTR-PM, with a thermal power of 100 MW employing a Rankine cycle for the electricity production.

It has the possibility of cogeneration of electric energy to improve the efficiency of the process. The connection of the HTR-PM with the model for obtaining hydrogen is done by employing an IHX type heat exchanger achieving an energy conversion cycle efficiency. The total efficiency of the iodine-sulfur process is calculated by making an energy balance in the proposed model and calculating the energy contained in the hydrogen produced. This efficiency value is in the range of those reported by other authors for theoretical and semi-empirical calculations. The proposed model is flexible because the Helium flow fraction of HTR-PM

dedicated to the production of electric energy can be modified, also modifying the capacity of the hydrogen production plant. The total efficiency of the SI process is determined as the ratio between the energy contained in the hydrogen ( $Q_{H_2}$ ) and the amount of energy consumed in the process, both thermal and electrical.

$$\eta_{SI} = \frac{Q_{H_2}}{H_{heat} + H_{elect}} = 37.53\% \tag{10}$$

The value obtained for the proposed model agree with the values published in the papers of the main research groups dedicated to this issue [5]–[7].

## 4. Conclusions

Analyzing the results obtained, we can conclude that the proposed hydrogen production methods have acceptable compatibility with the 2x250MWth project of the HTR-PM reactor. Both proposed systems had high efficiency values, appropriate for large hydrogen production. The computational model developed can be also used for furthers works, such as the hydrogen cost estimation and other sensitivity and sizing studies. All the energy efficiency values of the analyzed systems present values in the expected range and reported in several similar works.

## Acknowledgements

The authors would like to thanks FACEPE (Fundação de Amparo a Ciências e Tecnologías do Estado de Pernambuco) for the financial support for this investigation

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