DEVELOPMENT OF A CANDU SCWR AND COPPER CHLORIDE HYDROGEN CO-GENERATION MODEL

F. Ahmed[1], L. Lu[1, 2] and G. Naterer[1]
[1] Faculty of Energy Systems and Nuclear Science
[2] Faculty of Engineering and Applied Science, University of Ontario Institute of Technology, Oshawa, Ontario, Canada

Abstract

A model for the integration of the CANada Deuterium Uranium (CANDU) Super Critical Water Reactor (SCWR) with the copper chloride cycle to produce hydrogen fuel is proposed in this paper. In the copper chloride cycle, oxygen and hydrogen reactor require temperatures of 530 ˚c and 375˚c, respectively. These can be provided through the CANDU SCWR super heated steam outlet with temperature of 625˚c, and direct loop pressure of 25 MPa and regenerative loop pressure of 6 MPa.

1. Introduction

Super critical water fossil fuel power plants have been operating for a long time and the operating experience and design features can be adapted in the CANDU SCWR nuclear reactors. CANDU operational knowledge forms the basis of generation III and generation IV advance technologies including the ACR (Advanced CANDU Reactor) and the SCWR (Super Critical Water Reactor). The CANDU SCWR is advance reactor based on technologies such as the PWR (Pressurized light Water Reactor) and the BWR (Boiling Water Reactor) designs [1], operating at high temperature and pressure with opportunities of improved efficiency and reduced operational cost due to high thermodynamic single phase heat transport medium.

Various electrochemical processes [2, 3] for hydrogen production are identified and currently under review but very few have been found feasible. The methods and cycles which are proven viable for hydrogen production contain Steam Methane Reforming (SMR), Sulphur-Iodine (S-I) and Copper Chloride (Cu-Cl) cycles. The SMR cycle operates at higher temperatures from 700 to 800◦c and it is not free from carbon emission, whereas copper chloride hydrogen cycle operates at lower temperature i.e. 600◦c, and is also free from carbon emission. Hydrogen production using direct electrolysis and combination of electro-chemical process can maintain the nuclear plant efficiency by utilizing its wasted heat and is also a source of clean energy hydrogen fuel.

Significant efforts are currently underway to develop the hydrogen co-generation model by CANDU SCWR associated enabling technologies. The CANDU SCWR heat and steam is planned to be used for hydrogen production by copper chloride method which is increasingly viewed as a strong component of zero emission energy technologies. The SCWR is still in its evolution phase; therefore, collaborative efforts are required to better understand SCWR plant materials, chemistry, safety, reliability and stability methods. It is anticipated that SCWRs would have a combination of advantages of BWRs and PWRs [4].

This paper is organized into seven sections. In Section 2 the three thermal designs of CANDU SCWR is introduced. In Section 3, the P&ID diagrams of the copper chloride hydrogen production cycle are presented. The CANDU SCWR and CuCl hydrogen go-generation model is presented in Section 4. Concluding remarks are drawn in Section 5.

2. CANDU SCWR

Current SCWR research and development focuses on two different technologies. The pressure tube CANada Deuterium Uranium (CANDU) reactor design and the US pressure vessel Light Water Reactor (LWR) reactor design. In our model we use the CANDU Super Critical Water Reactor (SCWR) technology. Main features of CANDU SCWR system are higher thermal efficiency (45 to 50%) and simplified system configuration due to one phase superheated steam cycle that contributes to lower cost by elimination of certain equipments and thereby cheaper electricity. The CANDU SCWR primary heat transport system uses light water that operates at a temperature and pressure higher than 600^{o}c and 22.1MPa [5, 6].

The CANDU SCWR reactor design is based on two concepts, that is the conventional light water reactors (PWR) and the heavy water reactors (CANDU). The super critical steam generators and turbine design in conventional power plants spans over fifty years [7]. This experience of super critical turbines can be utilized effectively in CANDU SCWR systems. Previous studies were focused on conventional SCWR cycle for fossil fuel power plants but recently there has been a growing interest for the CANDU SCWR cycle [8]. Since CANDU SCWR concept is still in its evolution phase therefore several optimal configurations such as direct heat cycle, indirect heat cycle and dual reheat steam cycle can be investigated to form an efficient design.

The thermal designs currently under investigation are:

2.1 Direct reheat cycle

The reactor super critical steam is directly expanded to the high pressure turbine. Temperature is contained within the cycle. There is no need for expensive steam heat exchangers, dryers and moisture separators. However, high pressure turbine is directly exposed to the reactor steam, which can be a source of radioactive spread.

2.2 Indirect cycle

CANDU systems use the indirect method of steam expansion from reactor to the intermediate heat exchangers, dryers and separators. Thermal efficiency is sacrificed in indirect cycle but radiation containment is achieved through dual expansion cycle.

2.3 Dual reheat steam cycle

The parametric ranges achieved through regenerative loop can be up to 625 ^{o}c and 6.3 MPa. CANDU SCWR cycle efficiency is improved by employing regenerative heat mechanism within the SCWR reactor and also into the feed water system. The SCWR heat regeneration is accomplished by recirculation cycle between the HP turbine and the SCWR, which can achieve higher temperature steams at lower pressures. It is suitable for CANDU SCWR hydrogen co-generation model. Steam bleed from high pressure and low pressure turbines is led to feed water system heat exchangers to increase the feed water temperature up to 315 ^{o}c . Comparative analyses between no-reheat, single reheat and double reheat reveals that the single reheat CANDU SCWR cycle is optimal considering the design complexity and thermal efficiency of the cycle.

The major problem for integrating the hydrogen cycle into the CANDU SCWR cycle is the higher pressures of the SCWR heat transport cycle. The higher pressures are necessary to maintain the steam in the super critical state. The pressure ranges in SCWR with non-regenerative design is 25 MPa and 625 ^{o}c while it is from 9 to 6 MPa and 625 ^{o}c in the regenerative loop. In copper chloride cycle, the oxygen production, molten copper chloride unit requires 500 degrees centigrade while hydro-chloric cycle requires 430 ^{o}c. A lower pressure differential between the integration loops is essential to meet the safety requirements of both the CANDU SCWR and the hydrogen plant. Table 2.2.3 shows the CANDU SCWR hydrogen outlet temperature which is in the ranges from 600 to 625◦c and with pressures ranging from 25 to 6 MPa.

Table 1 Thermo /physical Parameters of CANDU-SCWR

Parameters	**Unit**	**CANDU-SCWR**	
Temperature (Reactor Core)	**^{o}C**	**Inlet**	**Outlet**
		350	**625**
Pressure	**MPa**	**25/6**	
Thermal Conductivity	**W/m-k**	**Inlet**	**Outlet**
		0.481	**0.107**
Temperature Increase (Inlet-outlet)	**^{o}C**	**275**	
Enthalpy Increase (Inlet-outlet)	**KJ/Kg**	**1943**	
Specific Heat	**J/Kg-K**	**Inlet**	**Outlet**
		6978	**2880**

3. Copper chloride hydrogen production

The copper chloride electrochemical hydrogen production cycle is divided into five major steps: Chlorination Step; Electrolysis Step; Drying Step; Hydrolysis Step; and Decomposition Step. As shown in Table 2.

Table 2 Thermo /physical Parameters of Cu-Cl Reaction

Reaction	→	Temp. °c
2Cu(s) + 2HCl	**CuCl (l) + H_2 (g)**	**430 – 475**
2Cu(s) + 2Cucl (Aq)	**CuCl (Aq) + Cu(s)**	**30 – 80**
$CuCl_2$(Aq)	**$CuCl_2$ (s)**	**30- 80 (crystallization) 100-260 (Spray Drying)**
$2CuCl_2$(s) + H_2O(g)	**CuO* $CuCl_2$(s) + 2HCl(g)**	**375- 400**
CuO* $CuCl_2$(s)	**2CuCl (l) + 1/2O_2 (g)**	**500 -530**

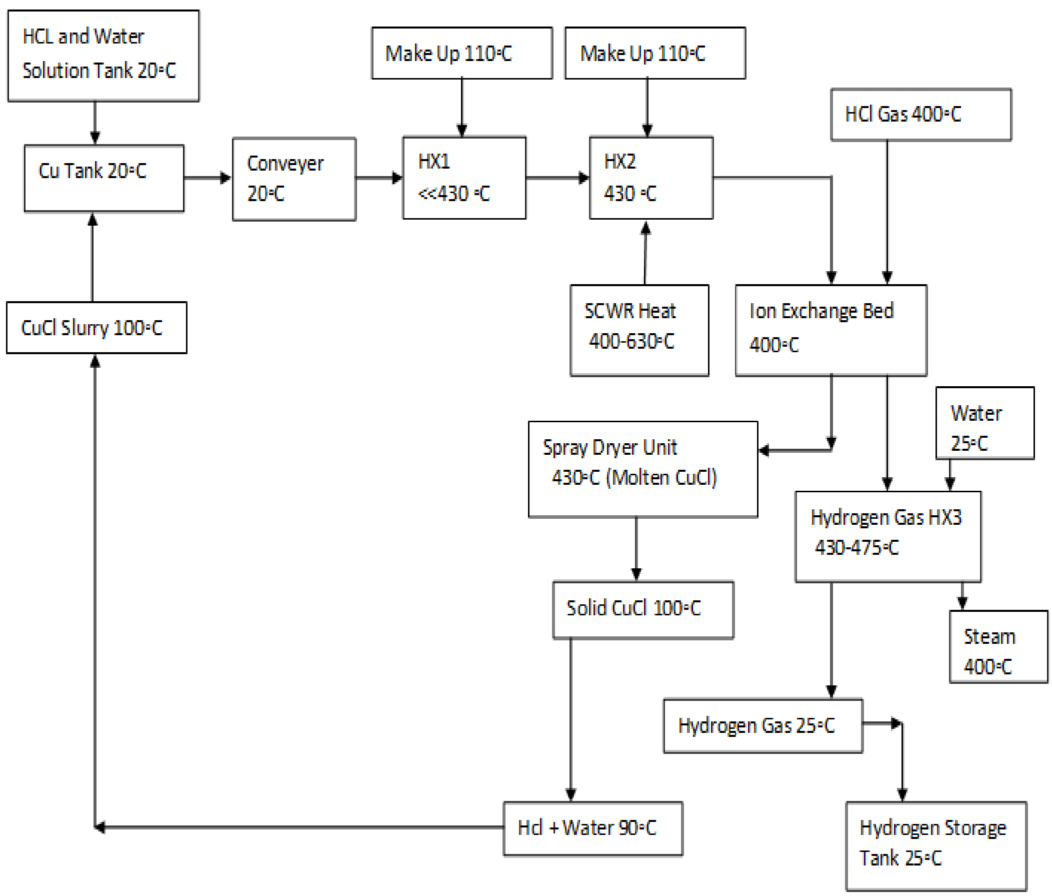

Figure 1 Hydrogen Production Loop

The chlorination step occurs at temperatures of 450-470 ◦c [9], producing molten copper chloride and hydrogen gas. The electrolysis step is accomplished in aqueous solution of HCl with temperatures between 30-80◦c. The endothermic drying step can be accomplished by crystallization with temperature ranging from 30-80◦c or by spray drying with temperature ranging from 100-260◦c. The hydrolysis step is accomplished at 375◦c. The final step involves endothermic decomposition producing oxygen at 530◦c. The chlorination and decomposition steps require higher operating temperatures from 470 to 530◦c. Therefore the CANDU SCWR high temperature and low pressure loop can be interfaced with chlorination and decomposition units. The following explains in detail of these two units.

Fig. 1 shows the one line diagram for the major components of close loop hydrolysis reactor. In this reactor the copper takes many forms that is solid, slurry and molten. In the hydrogen production unit (ion exchange bed) solid copper reacts with high temperature hydrochloric gas to form hydrogen and copper chloride. The hydrogen gas produced has temperatures from 430 to 475◦c, which is further cooled down to 25◦c by the cooling water and is passed through the purifier before storing it into the hydrogen storage tank. Molten copper chloride produced in ion exchange bed is spray dried to solid copper chloride and slurried with hydrochloric and water solution. The slurry is then pumped to the conveyer belt for the repetitive cycle. The cooling water exchanging heat with hydrogen gas enters heat exchanger at 25◦c and leaves it at 400◦c.

Fig. 2 shows the P&ID of the hydrolysis unit with supply lines, valves, non-return valves, flow-rater, temperature controllers and pumps.

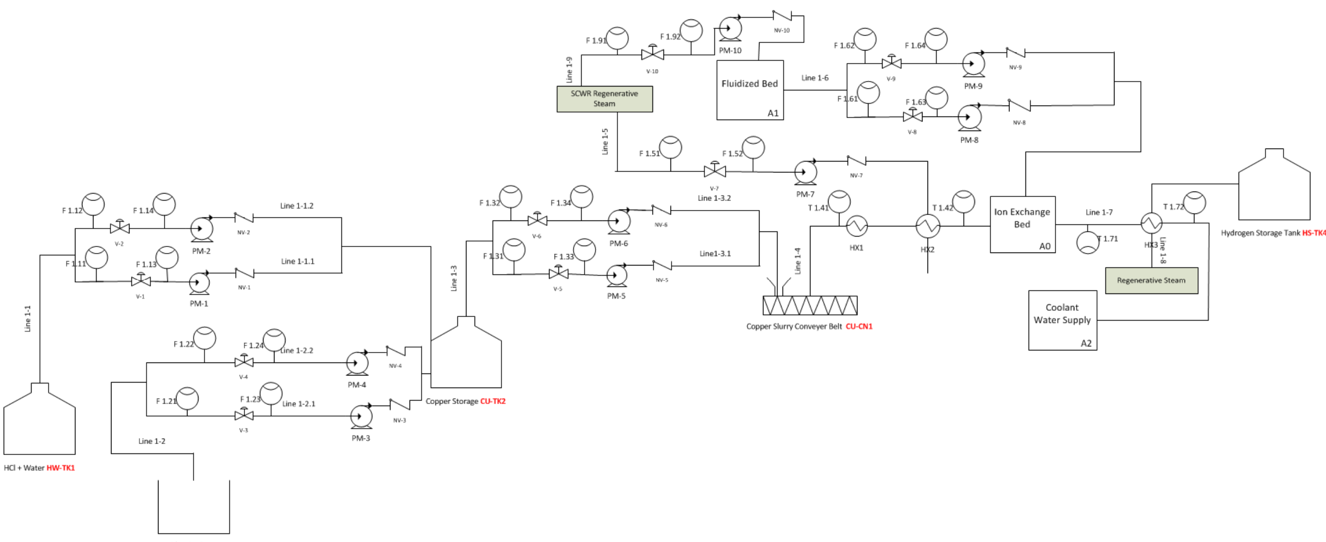

Figure 2 P&ID of Hydrogen Production Loop

Fig. 3 shows the single line close loop diagram of oxygen reactor unit. Oxygen is produced from cupric oxide copper chloride slurry ($CuO*CuCl_2$), Cupric oxide copper chloride slurry is heated to decompose into copper chloride and oxygen at 500◦c. The decomposition heat is provided by SCWR steam cycle. Oxygen at 500◦c is cooled down to 25◦c through coolant and stored in oxygen tank. The by product of reaction, molten copper chloride is cooled down up to 100◦C in spray dryer unit, and slurried with water and hydrochloric acid solution and stored in copper storage tank. Fig. 4 shows the P&ID of the oxygen reactor. Copper storage tank supplies copper to the sedimentation tank where it is mixed together with hydrochloric acid and water solution and this slurry is forwarded to fluidized bed. The copper chloride slurry is decomposed into hydrochloric gas and cupric oxide copper chloride.

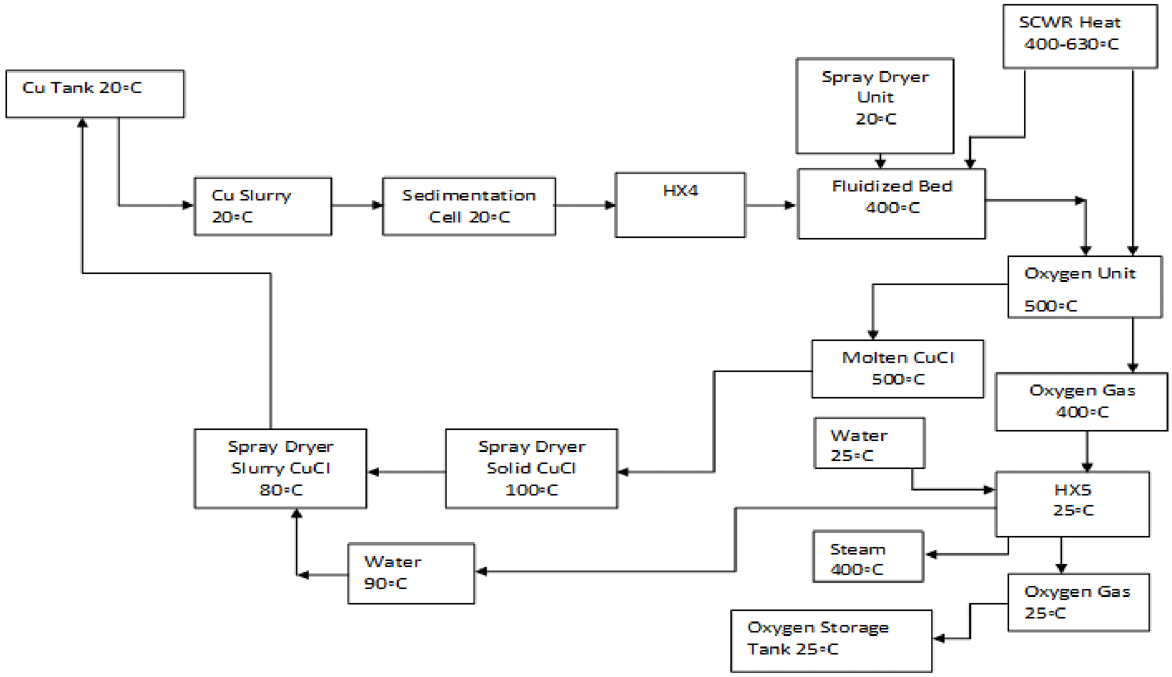

Figure 3 Oxygen Reactor Loop

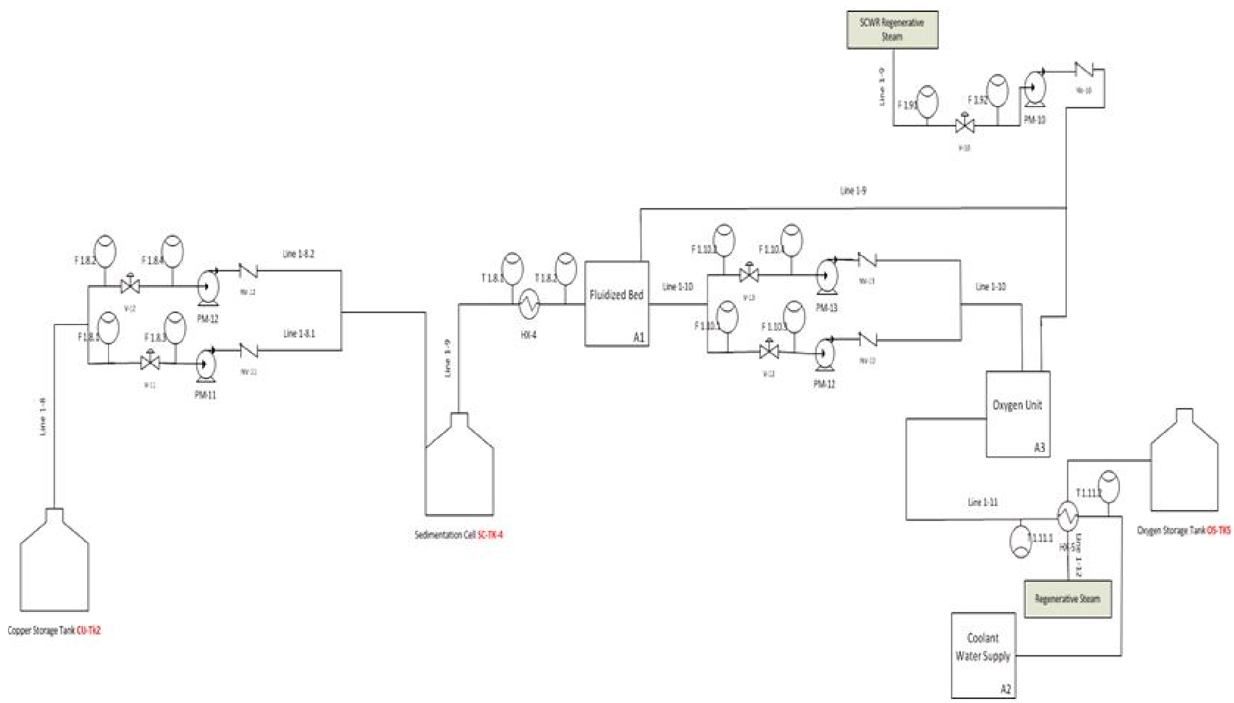

Figure 4 P&ID of Oxygen Reactor

4. Co-generation model

Figure 5 shows the one line diagram of CANDU SCWR and copper chloride hydrogen production unit integration. We assume two loops in CANDU SCWR reactor that is loop1 with high temperature and pressure; loop2 with high temperature and low pressure. Loop1 is the main heat cycle loop of the reactor and loop2 is the regenerative loop between HP turbine and SCWR. Both loop1 and loop2 heat can be utilized in copper chloride hydrogen production unit at oxygen production unit (500◦c) and fluidized bed (400◦c). The CANDU SCWR heat is expanded in these two loops. Oxygen gas is produced at high temperature; similarly hydrogen gas is also produced at high temperature and both are cooled down through heat exchangers. The regenerative heat produced in these steps can be utilized within the closed loop cycle and can meet up to 40-50% of Cu Cl loop heat requirement. The super critical intake steam is led through a pressure reducer via a pump to both the units of copper chloride hydrogen production plant. The intake lines from both the CANDU SCWR loops are isolated through two non-return valves.

To be more specific, the heat exchanger Hx2 in Fig. 1 uses the CANDU SCWR heat to raise the temperature of copper from 90◦c to 430◦c that reacts with high temperature HCl in the ion exchange bed to produce hydrogen gas. The CANDU SCWR heat is led into the fluidized bed in Fig. 3 and oxygen production unit that raise the unit temperatures from 20◦c to 400-500◦c..

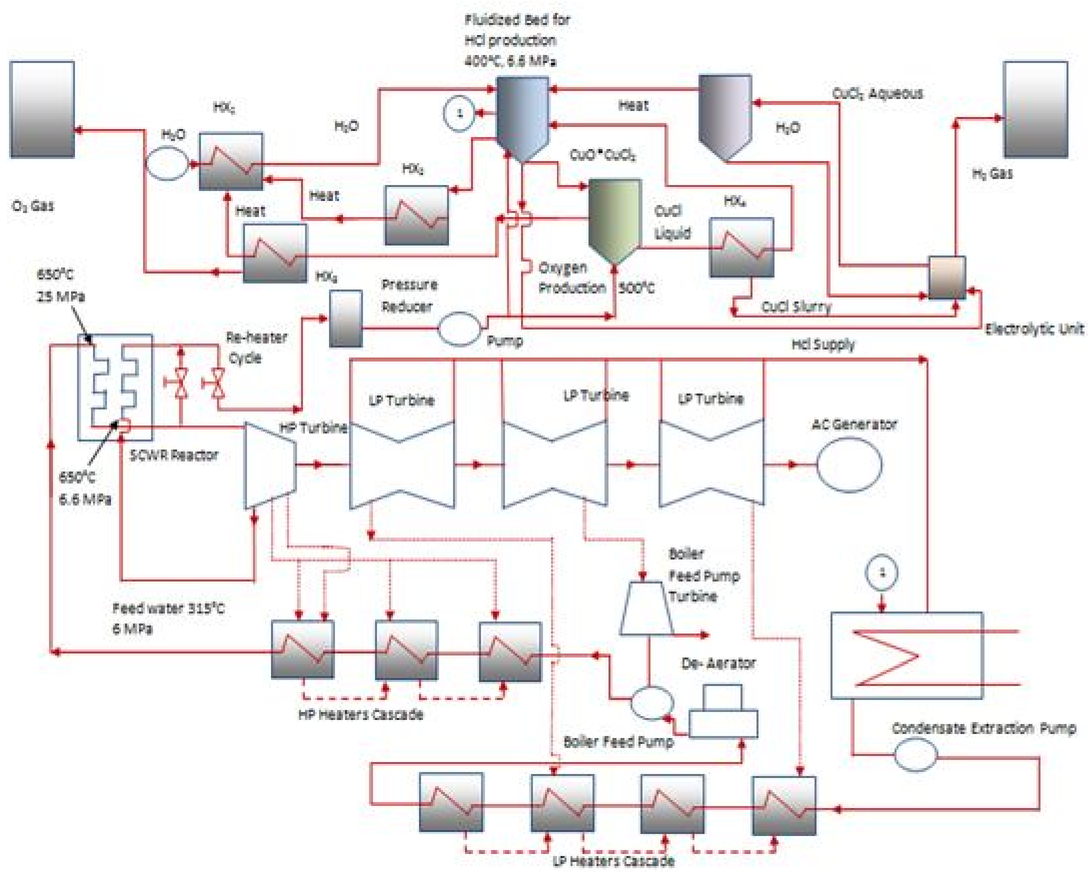

Figure 5 Schematic Diagram of Co-Generation of SCWR and CuCl Hydrogen Cycle

CANDU-SCWR design uses single/dual cycle, direct/indirect heating methods, but since thermal efficiency is higher in single cycle direct heating system therefore we assume our CANDU-SCWR design as single cycle direct heating model and we also omit the intermediate pressure turbine (IP) between the high pressure (HP) and low pressure (LP) turbines, assuming IP and LP turbines bearing the same efficiency. We also assume multiple stage single shaft turbine-generator cascade design for later stage steam expansion. The LP turbines in our model are double flow configuration turbine to handle the large amount of steam. Our CANDU SCWR hydrogen cogeneration cycle is comprised of: a super critical reactor, a supercritical turbine, which consists of one High-Pressure (HP) cylinder, and multiple Low-Pressure (LP) cylinders, one de-aerator, seven feed water heaters, and pumps. We also assume a regenerative method for reheating the steam leaving condenser hot well through cascade LP heat exchangers getting the sub-critical heat from LP turbines bleed valves. The same regenerative heating mechanism is adapted at the HP heat exchangers to attain the reactor inlet temperature of 350 ^{o}c.

5. Conclusion

In this paper, a CANDU SCWR and copper chloride hydrogen co-generation model is presented. Three thermal designs currently under investigation for the CANDU SCWR are presented. The one line diagrams and the P&ID diagrams for the hydrogen and oxygen reactors of the CuCl cycle are discussed. The schematic diagram of the co-generation model is presented.

6. References

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