

A New Industrial Hydrogen Production Process

Zina Meddeb*, Hatem Hajjem, Aicha Mabrouk, M. Razak Jeday

Research Unit: Energy and Environment, National Engineering School of Gabes (ENIG), Gabes University, Gabes, Tunisia

Email: zinameddeb1@gmail.com

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Abstract

This study was proposed to develop a new method for hydrogen production in significant amounts. It consisted in using sulfur dioxide (SO₂), and discharged from the sulfuric acid (H₂SO₄) production unit. This process could be considered as an alternative to many classical processes for air quality treatment resulting in a safer environment. Furthermore, it was an innovative method for hydrogen production. In fact, SO₂ was fed into a PEM electrolyzer stack. The dissolved SO₂ was oxidized at the anode which led to the production of sulfuric acid; whereas, hydrogen (H₂) was produced at the cathode. This new method was able to treat 3.7 t/day of SO₂ in order to produce 0.116 t/day of hydrogen and recover 5.6 t/day of 35 wt.% H₂SO₄. Results showed that the studied procedure was more economical in terms of energy consumption than the Westinghouse hybrid process. Hence, 67% of the energy needed for the decomposition step was reduced by our proposed process. After the presentation of the principles of the new process design, each part of the process was sized. The calculations showed that the number of electrolyzers could be calculated using the same formula used for the number of electrolyzers for water electrolysis or flux cell.

Keywords

Electrochemical Cycle, Electrolyzer, Environment, Hydrogen Production, Atmospheric Pollution, Sulfur Dioxide

1. Introduction

Sulfur dioxide is one of the most important pollutants of the atmosphere. It is clear that about 90% of the generated SO₂ comes from industrial plants. It has many negative effects on human health. Furthermore, this atmos-

*Corresponding author.

pheric pollutant generally acidifies rainwater, which involves the deterioration of forests, the erosion of materials and the acidification of soils and fresh waters. Hence, the removal of SO₂ from flue gases has received considerable attention and assumes significant importance over years due to its various deleterious effects to all forms of life [1]. Among the various physico-chemical wet and dry methods, wet scrubbing is considered to be the simplest and the most widely used process to prevent SO₂ emissions and minimize its level in the atmosphere. Nevertheless, the use of the scrubbing process does not meet the legislation requirements and remains a considerable problem [2]. Moreover, the main problems in the application of the wet cleaning are the non-desirable byproducts like waste water, which must be disposed of or recycled. Therefore, the objective of the present work is to introduce a new method for the treatment of sulfur dioxide released from effluents of the sulfuric acid production units and the production of a mass quantity of hydrogen. This latter is a non-toxic gas whose burning behavior is highly energy producing. In fact, the production of hydrogen is interesting in a sense that it does not only generate heat by direct combustion but also generate electricity in fuel cells, with residue water only. Fuel cells are the chosen field for the use of hydrogen and can be applied in portable electronic devices, transportation or buildings [3]-[5]. Hydrogen is produced from fossil fuels (oil, gas, coal) and from water by electrolysis or thermo-chemical dissociation. Currently hydrocarbons contribute with over 90% of the traditional hydrogen production with the predominance of natural gas, but these techniques result in the release of CO₂. However, because of the growing concern of the global environmental issues and the potential problems of energy resources depletion, it is highly desirable to produce hydrogen. In addition, electrolysis allows the mass production of hydrogen without greenhouse gases emissions.

This work presents a new process with two main goals. It treats SO₂ and produces hydrogen. Finally, this novel method is very promising in energy and ecological terms given that hydrogen is the main factor that will promote a new air clean development as well as renewable and sustainable energy.

2. Hydrogen Production Cycles

The hydrogen production cycles performed by dissociation can be categorized as [6]-[13]:

- Thermo-chemical hydrogen production: can be involved by direct dissociation of water or by a set of reactions at moderate temperature levels;
- Electrochemical: can be realized by conventional or high temperature electrolysis;
- Thermo-electrochemical: refers to the association of a low-potential electrolysis and one or more thermo-chemical reactions.

The Westinghouse hybrid cycle (Thermo-electrochemical cycle) was first proposed at Westinghouse Electric Corp. This method can be considered as a variant of sulfur-iodine cycle.

These processes consume 791 kJ of thermal energy per H₂ mol produced. Of this quantity 533 kJ is consumed by the decomposition step which reaches about 67% of the total energy consumed by the process [3] [9]. This is shown in **Figure 1**.

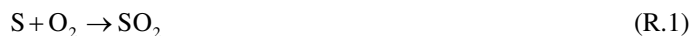
The hybrid sulfur process for the production of hydrogen using a high-temperature cycle is better than the water electrolysis.

3. The Novel Process

3.1. Industrial Sulfuric Acid Production Process

The sulfuric acid industrial production (H₂SO₄) was realized in three steps [14]:

- SO₂ production by combustion described in (R.1):



- Manufacturing SO₃ by a double absorption given in (R.2):



- Manufacturing H₂SO₄ as in (R.3):



But during the production of sulfuric acid there is always an emission of SO₂ into the atmosphere. Sulfur dioxide is an atmospheric pollutant which needs to be treated.

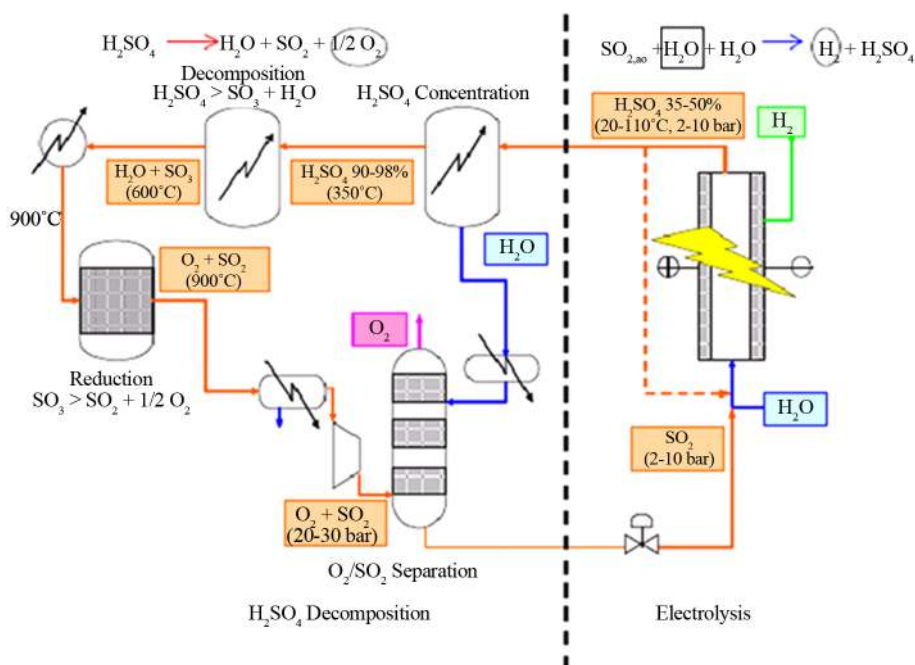
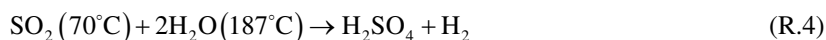


Figure 1. The Westinghouse hybrid cycle.

3.2. Using the Regenerated Sulfur Dioxide

The aim of this investigation was to integrate the electrolysis phenomenon after manufacturing the sulfuric acid in order to produce hydrogen in a massive quantity, to recover an amount of the produced sulfuric acid and also to eliminate the SO_2 emission discharged from the chimney into the atmosphere.

In this novel method the reactions of sulfuric acid decomposition performed at high temperature were eliminated since we used the SO_2 previously removed from the sulfuric acid production unit. Furthermore, reaction so f the sulfur iodine cycle were replaced by the sulfur dioxide electrolysis as presented by reaction (R.4).



In the electrolysis step, the sulfur dioxide was dissolved in an aqueous solution anodically oxidized; the hydrogen was produced at the cathode according to reactions (R.5) and (R.6):

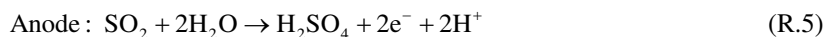


Figure 2 shows a schematic illustration of the new process.

4. Dimensioning of the New Process

4.1. Calculating the Amount of Regenerated Sulfur Dioxide

To calculate the amount of sulfur dioxide regenerated by the sulfuric acid production unit we had to achieve the molar balance of the entire process.

Data of the sulfuric acid process, such as the flow rates, temperatures and concentrations, etc. were taken from the industrial company (Tunisian Chemical Group).

For calculations, we assumed that [14]:

- The performance of the double absorption column method was 100%;
- The yield of the catalytic converter was of about 99.6%;
- The sulfur dioxide mole fraction at the furnace outlet was 10.85%;
- An output of the order of 1.500 t/d of the sulfuric acid was considered as a computing basis.

Figure 3 shows a block diagram of the double absorption process. Table 1 and Table 2 give the molar flow

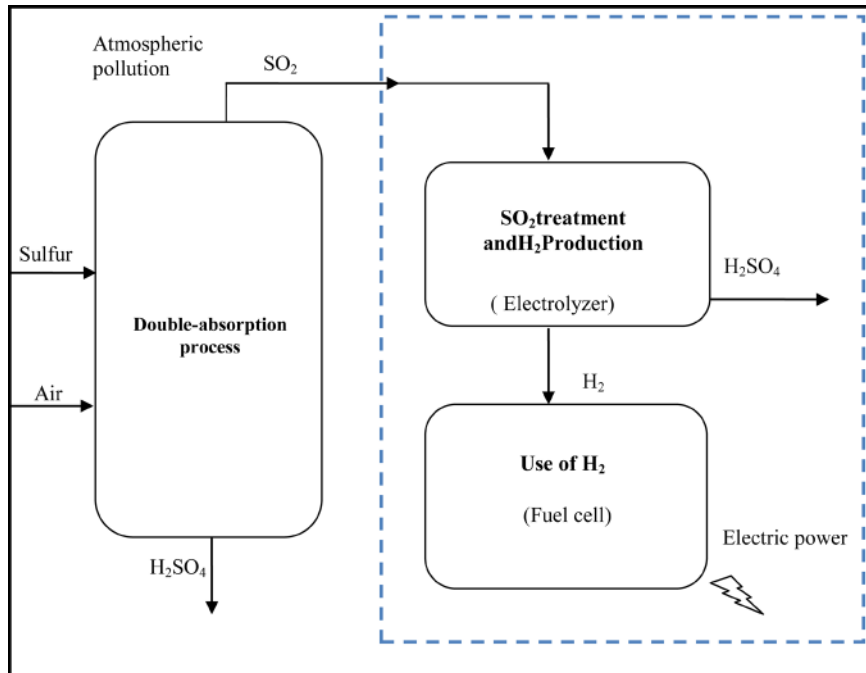


Figure 2. A schematic representation of the part added to the process of the novel.

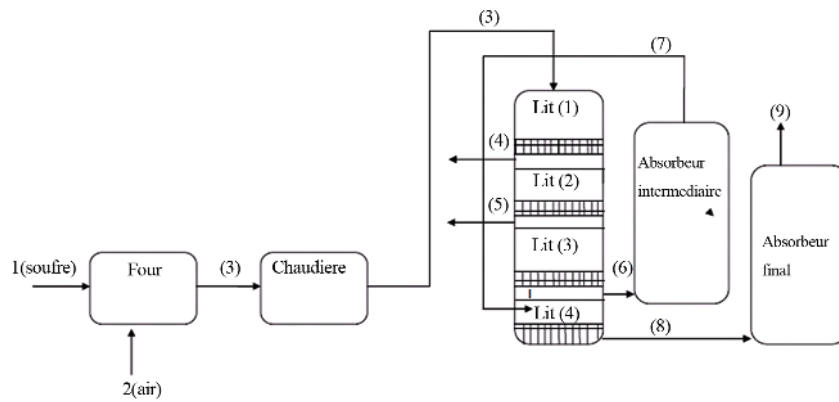


Figure 3. Schematic diagram of sulfuric acid production process.

Table 1. Molar flow entering and exiting the furnace.

	N_s	N_{O_2}	N_{N_2}	N_{SO_2}
Intel	$Q_s^{infurnace}$	$Q_s^{infurnace} (1+x)$	$Q_s^{infurnace} (1+x) \frac{79}{21}$	0
outlet	0	$N_{O_2}^{infurnace} x$	$N_{N_2}^{infurnace}$	$Q_s^{infurnace}$

inlet and outlet in the process.

$$N_{air}^{infurnace} = Q_s^{infurnace} (1+x) \left(1 + \frac{79}{21}\right) \quad (1)$$

x is the excess air calculate experimentally.

The molar flow rate of total gas outlet the furnace:

$$Q_{gaz}^{infurnace} = N_{O_2}^{infurnace} + N_{N_2}^{infurnace} + Q_{soufre}^{infurnace} = N_{air}^{infurnace} \quad (2)$$

Table 2. Molar flow exiting of beds and absorbers.

	N_{O_2}	N_{N_2}	N_{SO_2}	N_{SO_3}
Bed 1	$N_{O_2}^{out\ furnace} \left(1 - \frac{R_1}{2}\right)$	$N_{N_2}^{out\ furnace}$	$N_{SO_2}^{out\ furnace} (1 - R_1)$	$N_{SO_2}^{out\ furnace} R_1$
Bed 2	$N_{O_2}^{out\ bed\ 1} \left(1 - \frac{R_2}{2}\right)$	$N_{N_2}^{out\ furnace}$	$N_{SO_2}^{out\ bed\ 1} (1 - R_2)$	$N_{SO_3}^{out\ bed\ 1} + N_{SO_2}^{out\ bed\ 1} R_2$
Bed 3	$N_{O_2}^{out\ bed\ 2} \left(1 - \frac{R_3}{2}\right)$	$N_{N_2}^{out\ bed\ 2}$	$N_{SO_2}^{out\ bed\ 2} (1 - R_3)$	$N_{SO_3}^{out\ bed\ 2} + N_{SO_2}^{out\ bed\ 2} R_3$
Int abs	$N_{O_2}^{out\ bed\ 3}$	$N_{N_2}^{out\ bed\ 3}$	$N_{SO_2}^{out\ bed\ 3}$	$N_{SO_3}^{out\ bed\ 3} (1 - X_1)$
Bed 4	$N_{O_2}^{out\ absint} \left(1 - \frac{R_4}{2}\right)$	$N_{N_2}^{out\ absint}$	$N_{SO_2}^{out\ absint} (1 - R_4)$	$N_{SO_3}^{out\ absint} + N_{SO_2}^{out\ absint} R_4$
Fin abs	$N_{O_2}^{out\ absint} \left(1 - \frac{R_4}{2}\right)$	$N_{N_2}^{out\ absint}$	$N_{SO_2}^{out\ absint} (1 - R_4)$	$N_{SO_3}^{out\ absint} + N_{SO_2}^{out\ absint}$

R_1, R_2, R_3 and R_4 are respectively the conversion rate relative to SO_2 in the bed 1, bed 2, bed 3 and bed 4. X_1 and X_2 are respectively the rate of absorption relative to SO_3 in the intermediate absorber and final absorber.

The molar flow rate of total gas output the bed 1:

$$Q_{gaz}^{out\ bed\ 1} = N_{O_2}^{out\ furnace} \left(1 - \frac{R_1}{2}\right) + N_{N_2}^{out\ furnace} + N_{SO_2}^{out\ furnace} (1 - R_1) + N_{SO_2}^{out\ furnace} R_1 \quad (3)$$

The molar flow rate of total gas output the bed 2:

$$Q_{gaz}^{out\ bed\ 2} = N_{O_2}^{out\ bed\ 1} \left(1 - \frac{R_2}{2}\right) + N_{N_2}^{out\ four} + N_{SO_2}^{out\ bed\ 1} (1 - R_2) + N_{SO_3}^{out\ b\ 1} + N_{SO_2}^{out\ bed\ 1} R_2 \quad (4)$$

The molar flow rate of total gas output the bed 3:

$$Q_{gaz}^{out\ bed\ 3} = N_{O_2}^{out\ bed\ 2} \left(1 - \frac{R_3}{2}\right) + N_{N_2}^{out\ bed\ 2} + N_{SO_2}^{out\ bed\ 2} (1 - R_3) + N_{SO_3}^{out\ bed\ 2} + N_{SO_2}^{out\ deb\ 2} \quad (5)$$

The molar flow rate of total gas output the intermediate absorber:

$$Q_{gaz}^{out\ absint} = Q_{gaz}^{out\ bed\ 3} - N_{SO_3}^{out\ bed\ 3} X_1 \quad (6)$$

The molar flow rate of total gas output the bed 4:

$$Q_{gaz}^{out\ it\ 4} = Q_{gaz}^{out\ absint} - N_{O_2}^{out\ absint} \frac{R_4}{2} \quad (7)$$

The molar flow rate of total gas output the final absorber:

$$Q_{gaz}^{out\ absfinal} = N_{O_2}^{out\ bed\ 4} + N_{N_2}^{out\ bed\ 4} + N_{SO_2}^{out\ bed\ 4} + N_{SO_3}^{out\ bed\ 4} \times (1 - X_2) \quad (8)$$

Calculation results are presented in **Table 3**.

Therefore, the amount of the released SO_2 was about 0.669 mol/s for the double absorption process and was about 2.683 mol/s for the simple absorption.

4.2. The Electrolysis Section

The SO_2 treatment and the H_2 production took place in electrolysis section. The single electrolyzer is identical for the double or simple absorption process. But the total number of electrolyzers depends on the amount of SO_2 .

4.2.1. Single Electrolyzer

A single electrolyzer was studied, and then the results obtained were used to study the whole electrolysis system.

Table 3. Molar fractions calculation resultsto the double absorption.

Point	Flowrate (Kmol/h)	N ₂	O ₂	SO ₂	SO ₃	S
1	637.76	0	0	0	0	1
2	5770.17	0.79	0.21	0	0	0
3	5770.17	0.79	0.1	0.11	0	0
4	5578.84	0.82	0.07	0.04	0.07	0
5	5492.10	0.83	0.05	0.02	0.1	0
6	5464.35	0.84	0.045	0.005	0.11	0
7	4858.83	0.94	0.054	0.005	0.001	0
8	4847.01	0.94	0.053	0.001	0.006	0
9	4817.55	0.946	0.05	5E-04	6.2E-05	0

The electrolyzer used was of type PEM (Proton Exchange Membrane). Schematic of the electrolyzer system is given in **Figure 4**.

The following assumptions and conditions were used in the calculations:

- The membrane used was a Nafion 212;
- The conversion rate in the electrolyzer PEM was about 50%;
- The temperature was $T = 80^\circ\text{C}$;
- The pressure differential across the membrane was 600 kPa;
- The current density was 0.5 A/cm^2 ;
- The surface was $10 \text{ cm} \times 10 \text{ cm}$.

According to John A. [15]-[17], if the current density is 0.5 A/cm^2 , the potential is 0.71 V , the water flux production rate is $2.45 \times 10^{-5} \text{ mol/cm}^2 \cdot \text{s}$, and the sulfuric acid flux production rate is $0.25 \times 10^{-5} \text{ mol/cm}^2 \cdot \text{s}$.

Since the surface of the membrane was selected $10 \times 10 = 100 \text{ cm}^2$, then the number of moles of water flux production rate was $245 \times 10^{-5} \text{ mol/s}$ and the sulfuric acidflux production rate was $25 \times 10^{-5} \text{ mol/s}$.

Therefore, the sulfuric acid mass fraction can be found with a simple calculation. Under these conditions the sulfuric acid produced was 35wt.%.

Maximilian [9] [18] gave the SO_2 solubility in sulfuric acid as a function of acid concentration in system temperature 80°C and the pressure is 1 bar. The solubility was found to be of 0.71 g SO_2 per 100 g sulfuric acid solution. Accordingly $0.833 \times 10^{-5} \text{ mol/s}$ were drawn into $25 \times 10^{-5} \text{ mol/s}$ sulfuric acidflux production rate. **Figure 5** shows a schematic of the electrolyzer model.

Since the SO_2 conversion rate was 50%, then the number of moles of SO_2 at the entrance of the electrolyze was the double of the amount which reacted. So the SO_2 molar flux at the entrance of the electrolyzer was $50 \times 10^{-5} \text{ mol/s}$. In the former $0.83 \times 10^{-5} \text{ mol/s}$ dissolved in sulfuric acid and the rest $24.16 \times 10^{-5} \text{ mol/s}$ remained outside the electrolyzer at gaseous state.

Figure 5 shows the different flows at a single electrolyzer cell and **Table 4** shows a molar balance.

4.2.2. The Total Number of Electrolyzers for the Double Absorption Process

The total number of electrolyzers ($n_s n_p$) was the ratio of the total number of moles of SO_2 (0.669 mol/s) per the number of moles of SO_2 by a single electrolyzer ($25, 84 \times 10^{-5} \text{ mol/s}$). The result of the calculation was $n_s n_p = 2589$ electrolyzers.

Using the Equation (9) applied to the water electrolysis and the fuel cell [19] to compute the total number of electrolyzers:

$$v_{\text{H}_2} = \frac{n_s n_p I_{\text{cell}}}{2F\eta_F} \quad (9)$$

v_{H_2} is the hydrogen generation rate (mol/s), I_{cell} is the electrolyzer cell's current (A), F is the Faraday constant, 96487 (C/mol) , n_s is the number of electrolyzer cells connected in series, n_p is the number of parallel string of electrolyzer cells and η_F is the Faraday's yield.

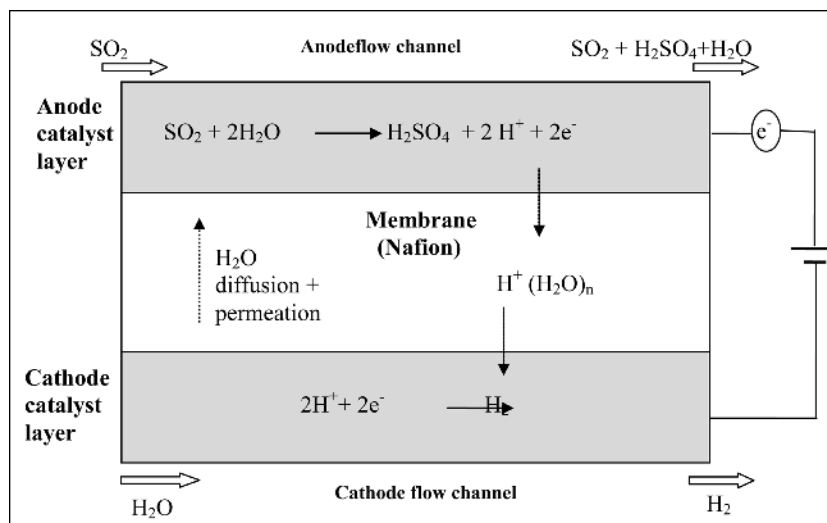


Figure 4. Schematic of the electrolyzer model.

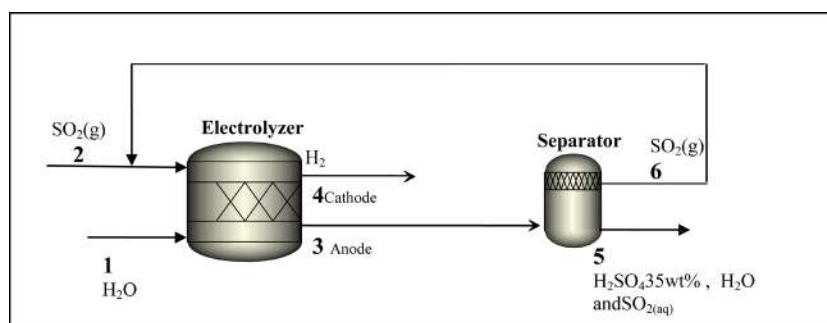


Figure 5. The different flows at a single electrolyzer cell.

Table 4. A molar balance at a single electrolyzer cell.

	H ₂ O mol/s	SO ₂ mol/s	H ₂ SO ₄ mol/s	H ₂ mol/s
1	295×10^{-5}	0	0	0
2	0	25.84×10^{-5}	0	0
3	245×10^{-5}	24.993×10^{-5}	25×10^{-5}	0
4	0.245×10^{-5}	0	0	25×10^{-5}
5	245×10^{-5}	0.833×10^{-5}	25×10^{-5}	0
6	0	24.16×10^{-5}	0	0

The total number of single electrolyzers was: $n_s n_p = 2582$.

This number seems very large. This is explained by the fact that the area of the membrane selected is low. But if the area is $100 \text{ cm} \times 100 \text{ cm}$ the number of electrolyzer is almost 26.

Almost the same total number of single electrolyzers was found by both methods. As a result, we can conclude that this equation can be applicable in hydrogen production by sulfur dioxide electrolysis.

For a single electrolyzer, the current was 50 A and the potential was 0.71 V [15]. To connect the electrolyzers we can for example place $(n_s, n_p) = (500, 5)$; with n_s is the number of electrolyzer in series and n_p is the number of branch in parallel. The total potential and the total current were determined as follows:

The total current (It) was equal to 355 V ($0.71 \text{ V} \times 500 \text{ elec} = 355 \text{ V}$);

And the total potential (Ut) was equal to 250 A ($50 \text{ A} \times 5 \text{ branch} = 250 \text{ A}$).

4.3. Sizing the Solar Panel

The characteristics of the chosen photovoltaic module (NT-175U1), which was manufactured by the SHARP Company, are summarized in **Table 5**.

4.3.1. Number of Branches Mounted in Parallel

A photovoltaic cell is a current generator; hence the current in the branch remains constant regardless of the number of cells connected in series. To get a well-defined quantity of current, branches must be mounted in parallel. Indeed the number of branches mounted in parallel is the ratio between the desired total current and the current of a module. In our case, the number of branches (N_p) was equal to 51.

4.3.2. Number of Modules per String

The branch voltage is the sum of the modules voltages connected in series. In fact, the number of a photovoltaic cell in series (N_s) was equal to 10.

A method for optimal sizing of an electrolyzer directly connected to a PV module is the subject of further work.

In total we had to use 510 ($N_s \times N_p = 10 \times 51$) Solar Panel module (NT-175U1).

5. Conclusions

This new process is able to treat 3.7 t/d of the sulfur dioxide, to recover 5.6 t/d of 35wt.% sulfuric acid and to produce 0.116 t/day of hydrogen (in the double absorption process).

A hybrid sulfur process for the production of hydrogen using a high-temperature cycle is competitive with water electrolysis.

The sulfuric acid decomposition step which produces oxygen and sulfur dioxide, is performed at a high temperature between 400°C and 600°C. This step is estimated to consume as much as 67% of the energy requirement for the process. So its elimination is very beneficial.

The method of using sulfur dioxide generated by the sulfuric acid production process can not only eliminate the decomposition step of the two acids but it also treats the sulfur dioxide emissions into the atmosphere. The treatment of sulfur dioxide and hydrogen production is two important aims. The produced amount of hydrogen by this method is very large.

The total number of single electrolyzers obtained when we size the electrolyzer by the use of the experimental data is consistent with that obtained by the use of the equation of water electrolysis and fuel cell. So we can conclude that this equation can be applicable in a hydrogen production process by sulfur dioxide electrolysis.

A detailed economical and energetic analysis will be needed, including the cost of the electrolyzers and the solar panel. This will be the subject of a future study, which will quantify the cost of the H_2 production.

An alternative optimum sizing method will be suggested to track the maximum power points (MPP) of the PV naturally in directly connected PV/PEM electrolyzer.

Acknowledgements

The authors would like to acknowledge the accountable of the research in G.C.T. because it has allowed us to do measures inside the sulfuric factory and for his encouragement about this subject.

Table 5. Solar Panel module characteristics (NT-175U1).

Maximum power	175 W
The maximum power voltage (V _{pm})	35.5 V
Maximum power current (I _{pm})	4.95 A
The open circuit voltage V _{oc}	44.4 V
Current shorting I _{sc}	5.4 A

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