POLITECNICO DI TORINO

Master of Science program in
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Master's Degree Thesis

Pre-design of a hydrogen production system

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Un ringraziamento speciale alla mia famiglia.

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Abstract

One of the biggest challenges today is to produce large amounts of energy in a sustainable way, to limit global warming caused largely by primary energy resources consumption such as fossil fuels.

In recent years, much focus has been placed on hydrogen: it is an energy carrier that does not exist in nature in elemental form, consequently it must be extracted from other molecules (example: methane, water, hydrocarbons).

In this thesis study, carried out at the Enapter company, a pre-design approach for an Anion exchange membrane (AEM) hydrogen production system is carried out. The different components of the electrolyzer are analysed, including both the structural and mechanical part. Furthermore, the energy management is also considered. The objective is to observe the variation of some parameters as the operating conditions change and to find the best solution according to the installation requirements of the product with regard to gravimetric indexes, volumetric indexes and power consumption.

This study is therefore divided into several sections, starting with the analysis of an electrolytic model for hydrogen production, the size analysis of the components and the energy analysis of some of these latter.

The results obtained were validated and showed that proposed model can be adopted for the pre-design development of an AEM electrolysis system, able to determine the best configuration according to the required operating conditions.

1 Introduction

1.1 Hydrogen

Hydrogen is often referred to as the energy carrier of the future [1]. It is known that for the future the energy systems will have to be based on renewable fuels and not like nowadays mostly on the fossil ones, and the hydrogen can be one of the energy carriers to direct the world towards this goal. It can be considered an excellent alternative to fossil fuels as it is the most common element on earth and in the universe, it has the highest energy density per unit mass and if the correct technology is used it is 100% clean as it releases water during combustion.

As mentioned above, hydrogen is abundant, but the problem is that it is not easily accessible: it cannot be found pure in nature, so it must be produced, and this requires energy. Sometimes the production can cost more energy than the one derived from the combustion: that's why an essential requirement to produce the H_2 from the water splitting is that it derives from renewable energy systems, such solar energy. Other important difficulties are related to the efficiency with which the hydrogen is produced, the use in fuel cell and its storage[2].

Among them the storage of hydrogen, especially for mobile applications, is a very big obstacle. Compared to it, gasoline has some advantages: it has higher energy density compared to the compressed and liquid hydrogen (31.6 MJ/l vs 4.4 MJ/l and 8.8 MJ/l). Moreover, gasoline can provide energy al low temperature and provides excellent control of energy discharge, besides its filling time in the tank is really short. US Department of Energy (DOE) requirements for a hydrogen tank are:

- Hydrogen gravimetric density of 7.5 % mass.
- Volumetric density of 70 g/l.
- Operating temperature between 233 and 358 K.
- Minimum delivery 12 bar (1.2 Mpa);
- Fueling time of 3 minutes.

It's essential so to overcome the obstacles to make hydrogen a viable energy carrier, and these problems can be summarized in four points:

- Production: hydrogen has to be produced, ideally from the water splitting, and so its necessary productions methods that would consume the least amount of energy and provide ability to produce hydrogen renewably on large scale.
- Storage: fuel needs to be easily stored for use and transports.
- Power generation: when hydrogen is ready to be consumed it is necessary to do so in the most effective way, so the power generation needs to be efficient and lightweight.

- Safety: the use and storage of the hydrogen comes with some risks and for this reason is necessary to have some precautions and safety measures.

Other important aspects are production cost, durability, stability of operation and safety, and this can determine the success or failure of any of the proposed solutions for a part of the hydrogen cycle [2].

1.2 Hydrogen production

On our planet there are several potentials sources on hydrogen: the most abundant is water, but hydrogen can be obtained from hydrocarbons, either fossil fuels or biomass (Figure 1). If the first process is without emissions and it is green, the second way to produce has the same CO_2 emissions amount as burning coal and gasoline [2]. From biomass instead is carbon neutral, because the plants absorbed the CO_2 during their life and the same amount of it is emitted during the production of H_2.

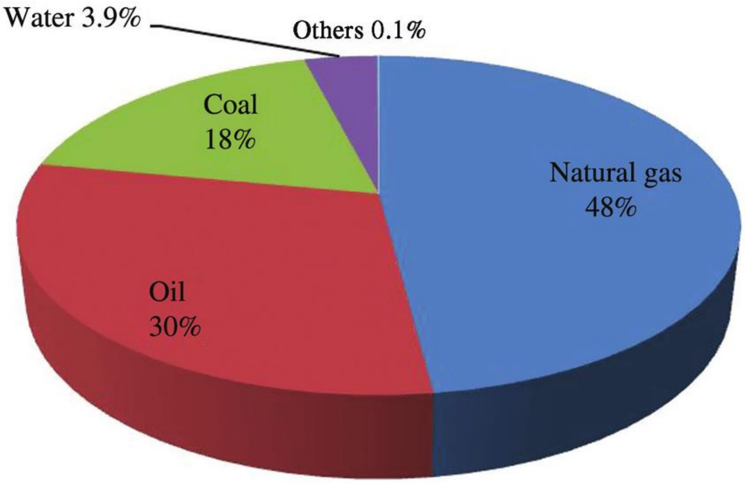


Figure 1: Source of Hydrogen production [2]

Production from fossil fuels

Now this is the main way to produce hydrogen for industries. The two sources from which it is produced are natural gas, which the process has around 80% of efficiency, and other hydrocarbons sources, with a varying degree of efficiency. The most used method for H_2 is the steam reforming: it works at high temperature (1000-1300K) and the water reacts with methane to yield syngas, which can be used to produce more hydrogen through reaction of water and monoxide. This process produces CO_2 wastes, that is a drawback.

Other processes are for example the partial oxidation of hydrocarbons, which includes partial combustion of fuel-air mixture at hight temperatures or in a presence of catalyst, which produces hydrogen and carbon black from hydrocarbons (no CO_2 waste) and coal gasification, where coal is converted to syngas and methane.

Biohydrogen production

Now biological H_2 production hasn’t found already industrial applications, but there are processes for conversion of biomass and waste streams into biohydrogen: some of them are like the ones described for the fossil fuels but it’s used biomass instead of fossil fuels.

The variety of pathways for biological conversion includes unicellular green algae, cyanobacteria, photosynthetic bacteria and dark fermentative bacteria [2]. It’s possible to use also solar energy conversion and the process is called photocatalyst, but the efficiency now is low and doesn’t exceed the 15%.

Production from water

Although many technologies have been tested to produce hydrogen from water splitting, these processes have not yet reached the desired efficiency needed for industrial applications. The positive side of this practice is that hydrogen is obtained in a pure way, without polluting and with no environmental impact. The cost of the resulting energy is also quite high compared to more traditional methods of energy production. The hydrogen produced by the electrolysis of water is less than 5% of the total. There are several methods of producing it through the cells: solid oxide electrolysis cell, alkaline electrolysis cell and polymer electrolyte membrane. The efficiency of typical electrolysis is around 50-80% when inefficiencies of production are not considered: considering this latter the efficiency can decrease to 35-40% for a typical nuclear or thermal power plant used as the power source, or even lower for a typical solar cell or array [2].

Another process is the thermolysis: this process is the thermal dissociation of water that happens at 2800 K in a spontaneous way. Now is very hard to use it in applications, but for the future the objective is to use it in solar concentrators or in nuclear plants, where hight temperature can be reached.

1.3 Electro-chemical cells

This chapter is going to define the theory which has been studied for the realization for this master thesis. There will follow a general introduction on the theory of the electro-chemical cells and then will be explained the electrolyzers.

1.3.1 Electro-chemical cell theory

The electrochemical cell (Figure 2) is a device that can convert chemical energy into electrical one and vice versa. Theoretically the electrochemical cell can run in both directions, and this depends on the Gibbs free energy: this quantity represents the thermodynamic potential, and this can determine the spontaneously of a process. Considering pressure and temperature constant, ΔG represents the available energy in the system that can be converted in work, and it is possible to assert that when $\Delta G<0$ the process is spontaneous, when $\Delta G>0$ is nonspontaneous and when $\Delta G=0$ the system is in equilibrium. As said before, this means that the electrochemical cell can be run in both directions:

- $\Delta G<0$ there's a power production, so the chemical energy is transformed to the electrical one;
- $\Delta G>0$ there's a production of chemical species and so the cell needs a power supply.

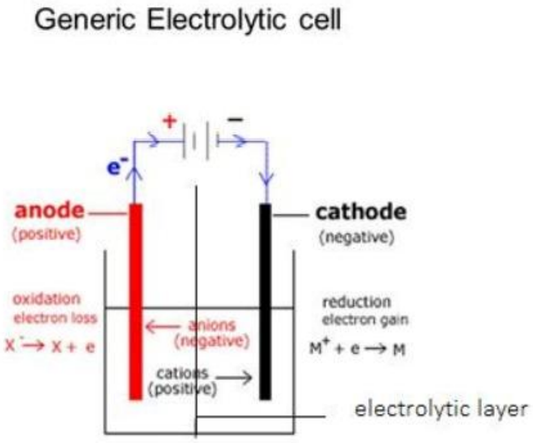


Figure 2: Generic electrolytic cell[16]

The electrochemical cell is composed by:

- Anode: is the electrode which drives the oxidation reaction
- Cathode: is the electrode at which the reduction occurs
- Electrolyte layer: it physically separates the two electrodes and inside there's the transition of the ions. It has to be characterized by a good ion conductivity and a good electrical resistance (the electrons have not to pass in the layer)
- External circuit: in this component there's the flow of the electrons

In the follow lines are represented the single reduction for anode oxidation, cathode reduction and the one for the global phenomena:

$$\mathrm{R_1 \leftrightarrow O_x + e^-}$$

$$\mathrm{R_2 + O_x + e^- \leftrightarrow P}$$

$$\mathrm{R_1 + R_2 \rightarrow P}$$

R_1 and R_2 are generic reactants, while P is a generic product.

The oxidation occurs in the anode and then the electrons and the ions move to the cathode, the firsts trough the external circuit and the seconds trough the electrolyte layer. In the reactions the charge separation occurred carry out the ions and this generates an electrical field.

When the external circuit is closed, a current I is generated by the flow of electrons and a power W_{el} is then generated thanks also to the voltage differential ΔV between the electrodes.

It is called galvanic cell a cell where the external circuit is closed, and all the Gibbs free energy is transformed in electrical power $W_{el.}$ The ions that pass in the cell are of different types, depending on the type of the cell: there are positive ions, that come from the anode and goes to the cathode (H^+), and negative ions, that goes from the cathode to the anode (O^{2-}).

When the external circuit of the cell is opened the cell is working in reversible conditions and transport phenomena doesn't occur. In this situation a voltage is measured, and it is called Open Circuit Voltage (OCV).

1.3.2 Fundamentals of electrolysis thermodynamics

Electrolysis is a non-spontaneous endothermic reaction (ΔG > 0); this means that it requires an external amount of energy to take place, be it electrical or thermal. Assuming for the moment that the reaction is reversible, the energy required for this process consists of the change in enthalpy between the products and reactants and can be calculated using the following thermodynamic law [13].

$$\Delta H = \Delta G + T * \Delta S \quad [1]$$

- ΔH: is the enthalpy variation between products and reagents. It is the total energy that has to be given to the system [J];
- ΔG: Variation of the Gibbs free Energy[J].
- T: temperature at which the reaction occurs [K].

- ΔS: is the entropy variation between products and reagents. It is the total energy that has to be given to the system [J/K].

The energy required for the process (ΔH) is formed by a thermal (T* ΔS) or electrical origin (ΔG). In standard conditions (25°C, 1bar) these parameters have the following values [13]:

$$\Delta\text{H}^0 = 285.88\ [\frac{kJ}{mol}]$$

$$\Delta\text{G}^0 = 237.23\ \left[\frac{kJ}{mol}\right]$$

$$T\Delta\text{S}^0 = 48.65\ [\frac{kJ}{mol}]$$

From the graph (Figure 3) is possible to see the trend of each term of the equations varying the operational temperature.

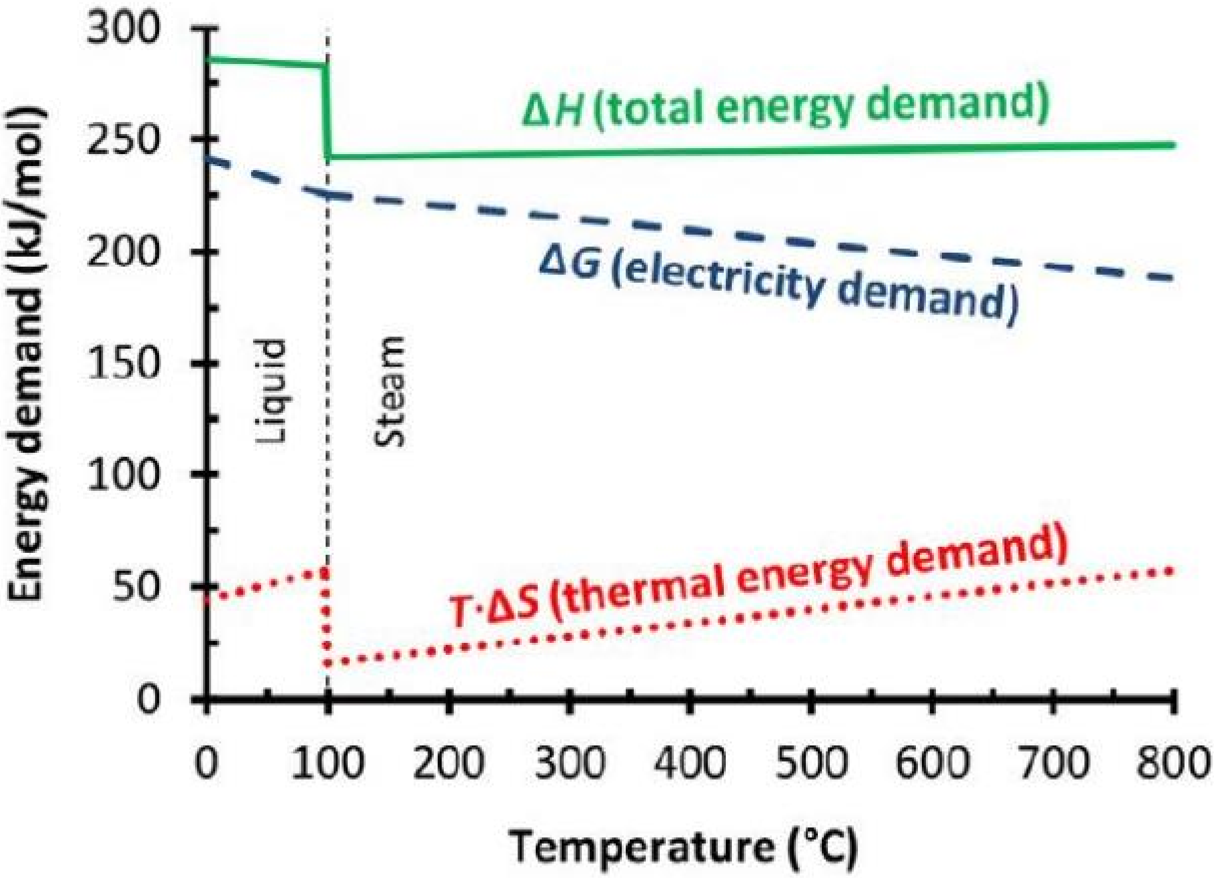


Figure 3: Energy demand for electrolysis [14]

The electrical energy demand Δg is reduced as the temperature T at which electrolysis takes place. It is greater after there is a phase change of water (100°C), i.e., when the electrolysis process takes place with steam: from the graph (Figure 3) the most significant change in $\Delta\text{H}\ e\ T\Delta\text{S}$ occurs when the water evaporates. Pressure, on the other hand, does not significantly influence the total energy required for the process (Δh).

The reversible cell potential difference U_{rev} is defined as the minimum potential difference potential required to be applied between the anode and cathode for electrolysis to take place [13].

From a thermodynamic point of view, the work required to carry out this process, at constant temperature and pressure, is equal to the increase in Gibbs free energy (ΔG).

If the electrolyser can only exchange electrical work, but not heat, the following equation is verified equation:

$$U_{rev} = \frac{\Delta G^0}{z*F} \quad [2]$$

- Z: number of electrons transferred during the electrolysis (in this case it is equal to 2 electrons);
- F: faraday's constant (96486 [C/mol]).

In standard conditions the reversible potential is equal to U^0_{rev} = 1.23[V].

The reversible potential, when the operating conditions are not the standard ones, is calculated using the Nerst equation:

$$U_{rev}[V] = U^0_{rev} + \frac{R*T}{z*F} * ln(\frac{\sqrt{P_{O2}}*P_{H2}}{a_{H2O}}) \quad [3]$$

- R: absolute gas constant (8.314 [J/kmol]).
- P_{O2} and P_{H2} are the partial pressures of the products of the reaction
- a_{H2O}: activity of the water.

Electrolysis can take place under adiabatic conditions, and therefore the energy required for the process Δh is only provided by the electric current. As with the reversible voltage, the change in enthalpy makes it possible to define the so-called thermoneutral potential U_{tn}[14].

$$U_{tn} = \frac{\Delta H^0}{z*F} \quad [4]$$

In standard conditions the thermoneutral voltage is equal to 1.48 [V]. The difference between the thermoneutral and reversible voltage is known as the thermal or entropic voltage and represents the minimum overvoltage with respect to the reversible voltage that must be applied to the electrolytic cell to initiate water dissociation. Under standard conditions, this potential is 0.25 V [14]. In the following figure (Figure 4) it is shown how the thermoneutral and standard potential varies with the temperature:

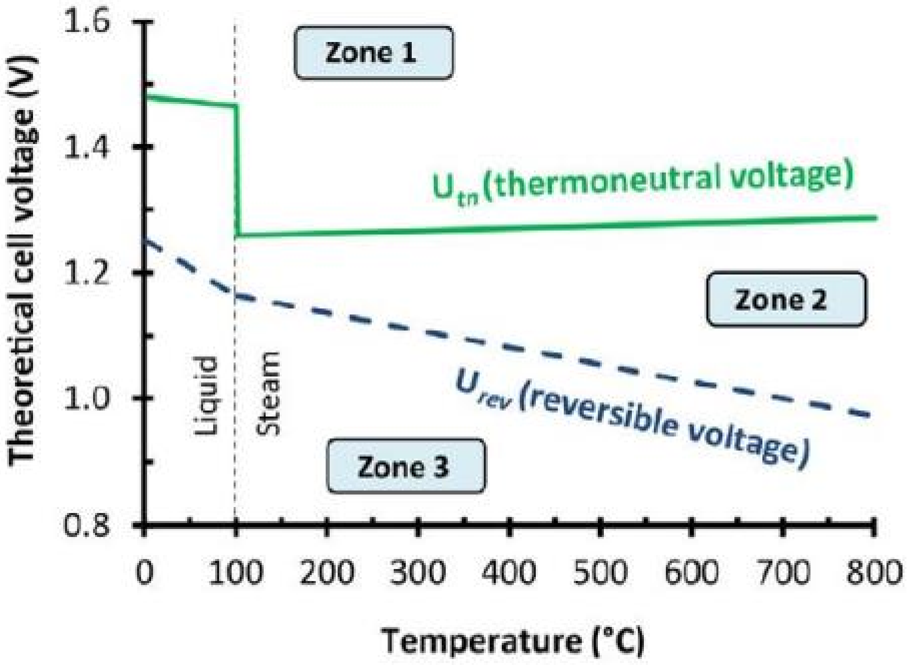


Figure 4: Theoretical cell voltage [14]

As can be seen, the thermoneutral voltage remains mainly constant (except for the water phase change point), and this is because the electrical energy is compounded by the thermal energy caused by the temperature increase

Three zones are identified in the figure:

- Zone 1: at a given temperature and pressure the voltage that is applied is higher than in thermoneutral: electrolysis takes place with an excess of energy, which is degraded into heat and must therefore be removed by a refrigeration system.
- Zone 2: this zone refers to the condition where the applied potential is between reversible and thermoneutral. The thermal energy supplied to make the electrolysis take place must have a value equal to the power associated with the delta between U_{tn} $U_{rev.}$
- Zone 3: in this case the voltage applied is lower than the reversible potential and so the electrolysis cannot happen.

If one considers the real case of an electrolytic cell operating at low temperatures, the potential is always higher than the reversible potential and the thermoneutral potential: this is due to the presence of irreversibilities due to the real electrolysis process, and these are called overvoltages. that are explained later.

1.3.3 Faraday's law

The Faradays' law gives the relation between molecular species (molar flow) of product and reactants and charged species (flow of current) of electrons and ions. The formula is:

$$n_i = \frac{I}{z_i \times F} \quad [5]$$

- n_i: molar flow $[\frac{mol}{s}]$ of chemical species i, both reactants and products
- z_i: charge number of chemical species i, it's the number of electrons involved in a oxidation or reduction process of the species i;
- F: Faraday's constant equal to 96478 $[\frac{C}{mol}]$

1.4 Electrolyzers

Electrolyzers are cell that operates in a reverse way ($\Delta G>0$) and so an electric power is needed. The most important reaction for the electrolyzers is:

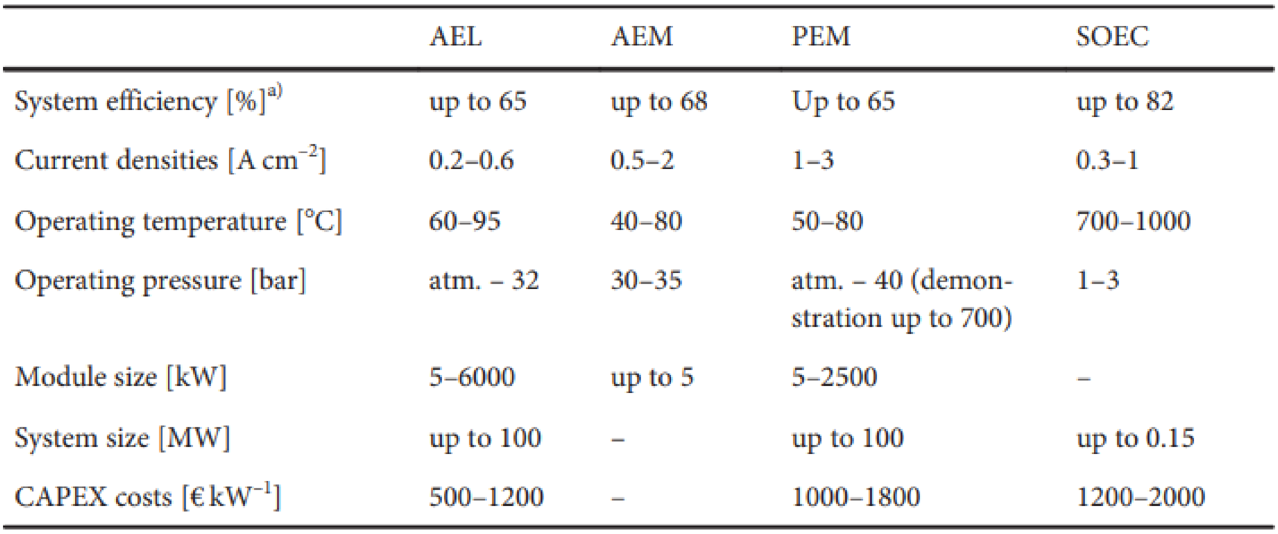
$$H_2O \rightarrow \mathrm{H}_2 + \frac{1}{2}O_2$$

This is one of the cleanest ways to obtain hydrogen: the power can be given from RES to produce H_2.

Basically, they are four types of electrolyzers dominating the market. The classification can be made based on the electrolyte, which dissociates into negative and positive ions and allows electric current to be conducted:

- AEC (Alkaline electrolytic cell): use an alkaline solution as electrolyte (liquid electrolyte, composition for example potassium hydroxide (KOH) 30%, or sodium hydroxide (NaOH)) in H_2O. Temperature has to be lower than 100 °C;
- PEMEC (PEM Electrolytic Cell): use Nafion as electrolyte, which is in solid from low temperature (lower than 80°C) and they have a different catalyst compared to PEMFC;
- SOEC (Solid Oxide Fuel Cell): there's a ceramic electrolyte (most used is Yttria stabilized Zirconia) and can work at very high temperature (700-850 °C).
- AEMEL (Anion exchange membrane electrolysis): this technology is a less-mature stage than PEMEC or AEL with only few companies so far working or commercializing it[3].

In the figure are shown the characteristics of the different types (Figure 5):



	AEL	AEM	PEM	SOEC
System efficiency [%]$^{a)}$	up to 65	up to 68	Up to 65	up to 82
Current densities [A cm^{-2}]	0.2–0.6	0.5–2	1–3	0.3–1
Operating temperature [°C]	60–95	40–80	50–80	700–1000
Operating pressure [bar]	atm. – 32	30–35	atm. – 40 (demonstration up to 700)	1–3
Module size [kW]	5–6000	up to 5	5–2500	–
System size [MW]	up to 100	–	up to 100	up to 0.15
CAPEX costs [€ kW^{-1}]	500–1200	–	1000–1800	1200–2000

Figure 5: Types of electrolyzers [3]

AEC

Alkaline water electrolysis is the oldest and mostly used technology to produce hydrogen. The AEL was used more where electricity was cheaper, the production from fossil fuel is not favourable and the hydrogen cost of transportation were too high. AEL dominates the market today and the sector is seeing a rise in research and development, to reach new requirements (high efficiency, cost reductions) adapting the classic design of the system.

Alkaline electrolytic cell consists of a cathode and an anode separated by a porous diaphragm: this layer doesn't permit the flow of electric charges and it prevents a mixing of the gases produced, but there is always a gas crossover. AEL usually uses as electrolyte the aqueous potassium hydroxide (KOH), or containing sodium hydroxide (NaOH), mostly with solutions of 20-30 % wt. because of the optimal conductivity and remarkable corrosion resistance of stainless stell in this concentration range [1]. The temperatures at which these type of cell works go from 70 to 100 °C and the pressure from 1 to 30 bar. The dimensions, the shape and the material used for AEL usually depends on the pressure of the system: for example, in systems that operates at the ambient pressure the active area of the working cell can be up to 3 m^2 and the shape is usually rectangular. The circular shape is mainly used for higher pressure levels, to facilitate an even distribution of the pressure along the whole area of the cell and therefore to prevent leakages [3] . But circular shapes cause a loss in materials due to the cutting up to 20% more.

One problem of this type of cell is the connection with renewable energy systems, as PV panels or wind energy: the ability of responding to fluctuations in electrical input is limited. This reason and to the fact that the gas purity is also lower than the one produced with the other method ensures that there is research to improve the performance of AEC. The cost also is quite high, due to the fact the catalyst is usually a noble metal.

The reactions that occur in this type of cell are:

- Cathode: $H_2O + 2e^- \rightarrow 2OH^- + H_2$
- Anode: $2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

AEM

The usage of the anion exchange membrane is growing in the last times, but it remains lower than the other three types. The power supply is connected to provide a DC supply to the cathode and to the anode. The working temperature depends on the material of the membrane, but it doesn't overcome 70 °C when the membrane is done with nickel oxide N_iO/N_iO. Schematically AEM has the same structure of the PEM cell, with the difference that the membrane transfer anions OH^- instead of protons H^+. The reactions are the same as the one that occurs in the AEC, with just some differences [4]:

- AEM electrolysis shows lower ohmic losses because it's thinner than traditional membranes.
- Membrane less expensive than PEM one.
- AEM can use similarly cost-effective materials while making much purer hydrogen at higher efficiency [15];
- It doesn't require platinum-group-metal (PGM) catalyst such as PEM cells, due to its basic condition. It is possible to use transition-metal catalysts with suitable performances, which makes it cheaper.
- AEM electrolyzer is fully scalable and is ideal for linking up with variable renewable energy sources because the AEC are comparatively slow at responding to a fluctuating power supply [15].

In the next table are shown some characteristics of AEM technology:

AEM	
Anode catalyst	Nickel-based
	Graphene
	Iridium-based
Cathode catalyst	Nickel-based
	Platinum
	Graphene
Membrane type	Nafion
	Tokuyama A-201
	Polysulfone
	Selemion AMV
Operational pressure	1-35 bar

Operational temperature	50-70 °C
Electrolyte type	KOH, NaOH

Table 1: AEM [5]

1.5 Polarization curve

The polarization curve represents the voltage of the cell as a function of the current produced from the device. As said before, when the cell is opened, and it is at equilibrium conditions the potential across the cell is the OCV: its value at ambient condition (temperature 25 °C and pressure 1 bar) is equal to 1.23 V. When the cell is closed, the system is no more in equilibrium and this process generates irreversibilities. The potential across the electrodes become:

$$V_c(T,P,i) = OCV(T,p) \pm Activation\ overpotential\ \pm\ Ohmic\ overpotential\ \pm Diffusion\ losses$$ [6]

It is possible to see below (Figure 6) that the polarization curve of the electrolyzers is not symmetric to the one of the fuel cells and this is due to the different catalysts used. So, the curve is not symmetric, also if the systems work apparently with the inverse way.

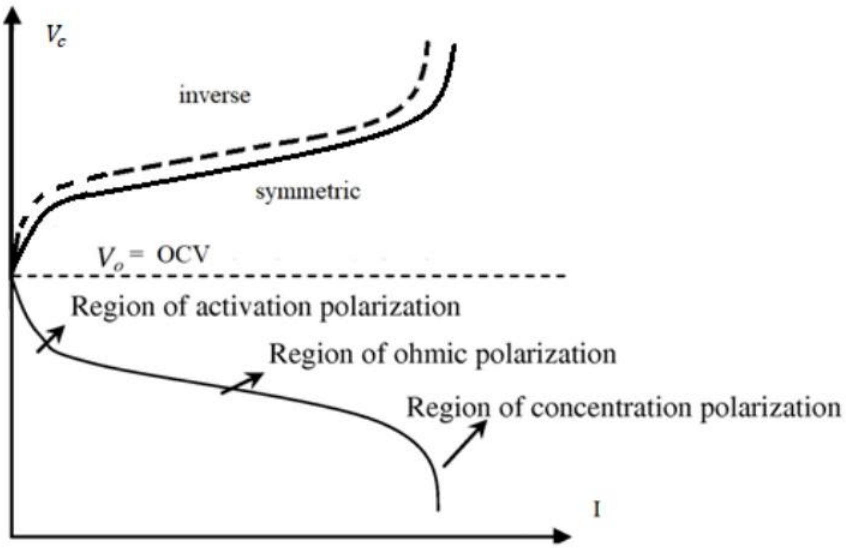


Figure 6: Polarization curve [1]

The regions are:

- Activation overvoltage (first region): is related to the activation energy of the reactions electrochemical reactions occurring at the electrodes. It is a loss caused by the limits of the speed of electrical charge transfer. Choosing a suitable catalyst and increasing the operating temperature can reduce the value of this overvoltage.

- Ohmic losses (second region): is related to the resistance to ionic and electronic transfer exerted by the electrolyte, the internal parts of the electrolytic cell and the contacts. It is proportional to the current density and depends on the type of material used, the geometries and temperature and can be calculated as the sum of several electrical resistances, according to Ohm's law.
- Concentration/diffusion losses (third region): considers the limits in mass transport mass transport that take place especially at high current densities. The products hydrogen (H_2) and oxygen (O_2) are not expelled as quickly as they are produced, so their concentration at the reaction sites and, consequently, the reaction kinetics decrease.

Knowing the voltage of the cell and considering a stack of cells, it’s possible to calculate the produced power:

$$W_{el} = n_c \times V_c \times I = n_c \times V_c \times i \times Area$$ *[7]*

Where n_c is the number of cells, i is the current density and the Area is the active area of the cell.

1.6 Models for alkaline systems

The cell stack is the heart of the system [6]. Thanks to the current sent to the stack, it occurs the decomposition of the water. The hydrogen and oxygen production are led with the electrolyte to the liquid-gas separation vessels, where the electrolyte is separated from the gas and returned to the stack by recirculating pumps [6]. Also, the KOH is recycled and so the electrolyte passes in a heat exchanger, where is cool down: this permits to remove the heat in excess and maintain the temperature in the cell.

1.6.1 Electrochemical model

This model can predict the electrochemical behaviour of an alkaline stack at different temperature and pressure conditions [6]. These latters have effect on the polarization curve, that analyses the different overpotentials that occur during the water electrolysis and calculate the voltage of the cell. The minimum voltage required for the electrolysis is equal to 1.23 V at standard conditions (1bar and 25°C) and it is known as reversible voltage; the cell voltage is always higher than the reversible one, due to kinetic and resistive effects.

Production is possible to measure thanks also to the Faraday’s efficiency, that is defined as the ratio between the moles of hydrogen produced and the theoretical ones. Also, the Faraday’s efficiency can be expressed as an equation, and it changes with the temperature, while the dependency on the pressure can be neglected because it has very little effects. Its values are usually in the 85-95 % range.

In the electrochemical model is also present the calculation of the diffusion of hydrogen into oxygen (HTO) and this depends on the temperature, but it doesn’t consider the pressure. This parameter is very important because the oxygen at the end of the process is sent to the atmosphere and if there's a high hydrogen concentration there could be problems, as flammability.

Mass balances

The hydrogen production rate at the cathode depends on the electrochemical behaviour of the cells and the consumption of water and the production of oxygen is determined in a stoichiometric way from the hydrogen produced. For an ideal alkaline system, the hydrogen produced is linearly dependent with the current sent to the stack by the PSU.

Energy balances

It's possible also to calculate the energy losses that occur in the stack. Firstly, it's important to define the total energy demand for electrolytic hydrogen production, that is given by the enthalpy of reaction: this is used to calculate the thermo-neutral cell voltage (V_{tn}). This means that if the potential of a cell is higher than the thermo-neutral one, no external heat is needed to carry out the electro-chemical reaction [6]. A part of the heat generated during the process is assumed to be lost in the environment. The heat makes the temperature of the stack increasing, and so a heat exchanger is needed to cool the fluid down.

System efficiency

This shows the energy efficiency of the system. It linearly depends on the energy that the hydrogen produced contained and in a non-linear way on the power sent to the stack from the PSU. It is possible to calculate the power of the stack, that is linearly dependent on the operational current and on the cells number.

1.7 Balance of plant components

The Balance of Plant is the set of auxiliary control and regulation equipment that the heart of the electrolyser, the stack, and the obtaining of the product gases under the required conditions.

PSU

Firstly, the process of the water splitting takes place in direct current (DC). This current is applied to the stack and so the electricity must be converted before sending it, due to the fact the electricity grids operate with alternating current [7]. The voltage of the stack depends on the number of the cells: when the cells are in series, the voltage linearly grows with the number of the cells. At the beginning of life, the voltage needed to produce hydrogen is lower, but with the passage of time due to the degradation of the electrolysis cells, the stack voltage must be increased. The stack current depends on the current density and on the area of the cell: the current is one of the most important parameters for the hydrogen production (they are linearly dependent).

Water purification

To avoid damages the cells it’s important to use as much as possible high-purity feed water [7]. So, every system must have a water purification unit, that ensure a low conductivity compared to the tap water and a fully deionized water. The most used water for systems is the tap water, but also the sea water or wastewater could be used doing pre-treatment and for this reason it would be more expensive. In the electrolysers it doesn’t go simple water, but the system is filled with liquid electrolyte solution (usually KOH).

Hydrogen purification

Compared to conventional hydrogen production processes like steam-methane reforming or coal gasification, hydrogen produced by water electrolysis processes has a high purity [7]. It can happen that the hydrogen contains small amount of oxygen, that goes into cathode from the anode. This impurity must be avoided because some applications need very pure hydrogen, otherwise components can be damaged. For this reason, a purification unit is usually inserted in electrolyser systems: it can be for example a deoxygenation reactor.

Cooling system

The process of electrolysis is not and ideal process and due to internal resistances in the cells heat is generated in the stack. So, this heat must be removed, to not damage the components of the stack and the cell itself: a heat exchanger is placed in the circulation cycle [7]. The gases produced are also cooled to condense the water, that can be sent again to the electrolysis system to reduce the water demand. The heat must be removed also from the compression system and from the gas purification.

Compression unit

To use it, the hydrogen must be compressed: in relations to the applications, a final pressure must be between 80 and 900 bar [7]. This is due the fact that at ambient conditions the energy density of the hydrogen is low and taking also into account the storage, transportation, and further processing, this would not be an option. To have a good energy density the hydrogen must be compressed at high pressure and usually this is done thanks to a multi-stage compressor: this is done typically to limit the temperature after each stage of the compression (usually the compression ratio is maximum equal to 3). The capacity of the compression system can vary from some kW to also MW range.

Pumps

There are different types of pumps in the plant:

- Circulation pumps: permit the circulation of water reactant on the anode side and the reintroduction of KOH separated from the product gas into the circulation circuit [15];
- Feed pumps: increase the water pressure to the pressure of the anode side and feeds it to the process and they're necessary to maintain the concentration of the alkaline solution at a constant level[15].

Power electronics

The electrolysis happens when direct current (DC) is applied to the stack. The power electronics consists of a transformer and rectifier and convert the incoming AC power into a regulated DC current, which is applied to the contacts of the stack [15]. Usually thyristor-based rectifiers are used to convert from AC to DC and they can work with high current, so can be suitable for most stack sizes. For what concern the voltage, the degradation of the electrolysis cells has to be taken into account and so an higher voltage at the end of the life is needed.

1.8 Gases/liquid

Hydrogen

Hydrogen is one of the products of the electrolysis. It has different properties:

- It doesn't have colour and odour.
- It is easy inflammable;
- Very reactive gas, especially with oxygen.
- It's lighter than air;
- It has the ignition temperature at 500°C.
- Lower heating value (LHV) of 120 MJ/kg, higher than gas (43.5 MJ/kg) and methane (50 MJ/kg).

The main problem for electrolysers and systems that product hydrogen are the leaks of this gas: since it's lighter than air, in a close environment it accumulates on the top of it and so there's an increase of risk of explosion: it is necessary just a hot surface or a spark to generate an explosion. For this reason, it's important to have a sensor to detect leaks and it must be ensuring a change of air in the environment where the H2 is produced. The hydrogen also causes the embrittlement of some materials, leading to damages on metallic and non-metallic components.

Oxygen

The oxygen is the other product from the electrolysis. It has the following properties:

- No colour, no odour, and no taste.
- Highly reattive;

- It is an oxidizing, so with materials it reacts forming oxides.

It is the promotor of the combustion: the process to happen needs an ignition, that could be heat or a spark. The oxygen has the highest energy rate that is released during the process, even if it’s an oxidant and not a fuel. If the oxygen is present in a big quantity in the environment and its partial pressure is increased it can cause damages to the human body, as in the case of hyperoxia, an excess of oxygen in the body tissues. This can lead to neurologic and pulmonary problems, and the eyes can be affected by it.

Potassium hydroxide

The potassium hydroxide is a white solid component. It is very soluble in water and mixed with the water forms the electrolyte. It is very dangerous when it meets the skin, eyes, ingestion, or inhalation. The contact with the skin leads to inflammation of it, while with inhalation there could be irritation to the respiratory part.

The potassium hydroxide is corrosive, and it is usually handled in steel, nickel, or certain type of plastic equipment. To store the potassium hydroxide solutions are used materials and black iron or mind steel.

2 Mathematical model for Alkaline electrolyzer

The aim of this model is to simulate the electro-chemical behaviour of an alkaline system, based on the polarization curve and faraday efficiency as function of the current density under different operating conditions, such as temperature and pressure [8] (Figure 7). The system considered works with an alkaline aqueous solution of 1-3 wt% KOH as electrolyte, with an operating temperature of 50-60 °C and a pressure of 30-33 bar.

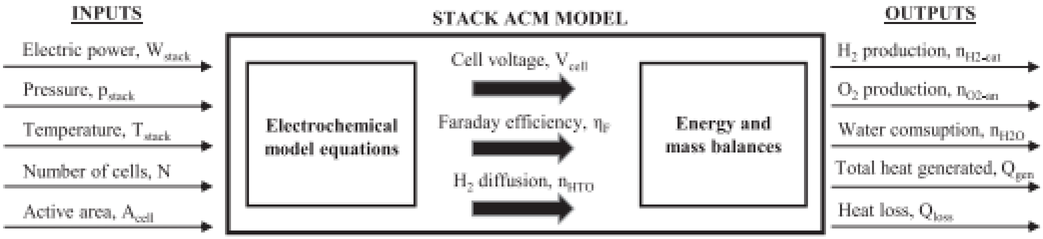


Figure 7: Stack model [8]

2.1 Polarization curve model

The electro-chemical behaviour of an alkaline system is described by the polarization curve and the voltage of the cell is equal to the sum of the reversible voltage and overpotentials [8]: the reversible voltage is calculated trough the Nerst equation at standard conditions (1bar, 25 °C), while the activation overpotentials can be estimated by the Butler-Volmer equation and finally the Ohmic overpotentials can be calculated with the Ohmic law (i * R).

The polarization curve can be described using a semi-empirical current- voltage model. The final equation of this model is the following one, in which pressure, temperature and the current density affect the voltage of the cell:

$$U_{cell} = U_{rev} + [(r_1 + d_1) + r_2 * T + d_2 * p] * i + s * log[(t_1 + \frac{t_2}{T} + \frac{t_3}{T^\wedge 2}) * i + 1]\ [8]$$

U_{rev}: reversible voltage of the cell [V]

i: current density [A/cm^2]

T: operational temperature [°C]

P: operational pressure [bar]

The parameters of the equations are:

- Parameters of the activation overpotentials:

  - $t = t_1 + \frac{t2}{T} + \frac{t3}{T^\wedge 2}$, that depends on the temperature

  - s: that is usually considered as a fixed term

- Parameters of the Ohmic overpotentials:
  - $r = r_1 + r_2 * T$, depends mainly on the temperature
  - $d = d_2 + d_2 * p$, represents the variation based on the pressure

r_1, r_2, d_1, d_2, s, t_1, t_2 and t_3 are obtained from experimental data [8] and from the Ulleberg's model, and the values are shown in Figure 8.

Model	Coefficient	Value	Unit
Polarization curve	r1	4,45E-05	Ω m^2
	r2	6,89E-09	Ω m^2/°C
	s	0,33824	V
	t1	-0,01539	m^2/A
	t2	2,00181	m^2 °C/A
	t3	15,24178	m^2 °C^2/A
	d1	-3,13E-06	Ω m^2
	d2	4,47E-07	Ω m^2 bar^-1
Faraday efficiency	B1	4,50E-05	-
	B2	1,021	-
	B3	-247,46	A m^-2
	B4	2,069	A m^-2 °C^-1
	B5	-0,035	A m^-2 °C^-1

Table 2: Model coefficients [8]

To obtain the total voltage of the electrolyser is necessary to multiply this value (U_{rev}) for the number of the cells of the stack.

Faraday efficiency model

In an electrochemical process the gas that is produced can be proportional to the electrical charge consumed by the cell: this is what is described by the Faraday's law. In an ideal process the electric charge is directly proportional to the amount of hydrogen produced, so it's possible to calculate the effectiveness of the process using the Faraday efficiency to have a comparison between the number of moles of hydrogen produced and the theoretical ones that should have been produced. Usually, the Faraday efficiency is in a range of 85-95 %. Using an empirical model Hug et all [8] efficiency is calculated using a model based on 5-parameters, in which the pressure is not considered due to the fact it shows very small effect in the pressure range that is considered in this situation.

$$eta_f = B_1 + B_2 * exp\left(\frac{B_3 + B_4 * T + B_5 * T^2}{i}\right) \quad [9]$$

This formula is valid at any temperature and the constants B are demonstrated in an experimental way [Figure 8]. When the current in becoming smaller, the efficiency is smaller too: this means that smaller is the current density, smaller is the hydrogen produced, as it will be possible to see in the Mass balances.

Mass balances

From these experimental models is now possible to do the mass balances of the system:

- The hydrogen produced depends on the electrochemical behaviour and on the Faraday efficiency of the cell:

$$nH_2, prod = eta_f * \frac{I}{z*F} * Ncell \quad [10]$$

  Eta_f: Faraday efficiency

  I: cell current

  Z: number of electrons of H2 that takes place to the reaction

  F: Faraday number

  Ncell= number of cells

- The oxygen production and the water consumption are calculated trough stoichiometric reaction:

$$nO_2, prod = \frac{1}{2} * nH_2prod \quad [11]$$

$$nH_20 = nH_2, prod \quad [12]$$

System Efficiency

Once all these terms are known, it’s now time to calculate the efficiency of the performance of the system: the energy efficiency of the process is the ratio between the energy contained in the useful product and the energy of the input streams. The formula is the follow one:

$$eta = nH_2, out * \frac{LHVH_2}{W_{net}} \quad [13]$$

- n_{H2}, out: flow of H2 produced [kg/s]
- LHV_{H2}: lower heating value of the hydrogen [J/kg]
- W_{net}: electric power input from the PSU [W]

W_{net} is composed by W_{stack}, that is the electric power input for the stack operation, and all the other components that need energy, as the recirculating pump.

The power of the stack can be calculated as follow:

$$W_{stack} = V_{stack} * I = (V_{cell} * N) * (i * A_{cell}) \quad [14]$$

- V_{stack}: voltage of the stack, is equal to the voltage of the single cell (V_{cell}) multiplied by the number of cells.
- I: current of the stack, equal to the current density (i) multiplied by the active area of the cell (A_{cell}).

3 Electrolyte

3.1 Electrolyte properties

In this chapter the properties of the electrolyte are studied, thanks to the model of an alkaline water electrolyzer cell[9].

In the model are calculated the electrolyte transport properties such as density, viscosity, heat capacity and thermal conductivity, depending on the operational temperature and on the percentage of KOH in water. The different equations for the properties are taken from different authors of the article, trying to figure out which experimental data were the best for each property, studying the values and the graph trades of them. All the calculations are done at the operational temperature of the stack (T=55°C) and at ambient pressure, while the percentage of the electrolyte varies from 0-3 wt %: 0% it's pure water, 1% is when the tank is full of electrolyte, while 3% is when the electrolyte in the tank is at the minimum level and its refill is needed.

Density

The density of the electrolyte is calculated with the following formula [9] and the results are shown in Figure 9:

$$rho = (K_1 + T * K_2 + T^2 * K_3) * 10^{((K_4 + K_5 * T) * Y_i)} \quad [15]$$

$K_{1,2,3,4,5}$: constant of the density equation

T: operational temperature in °C (55°C)

Y: mass fraction of KOH

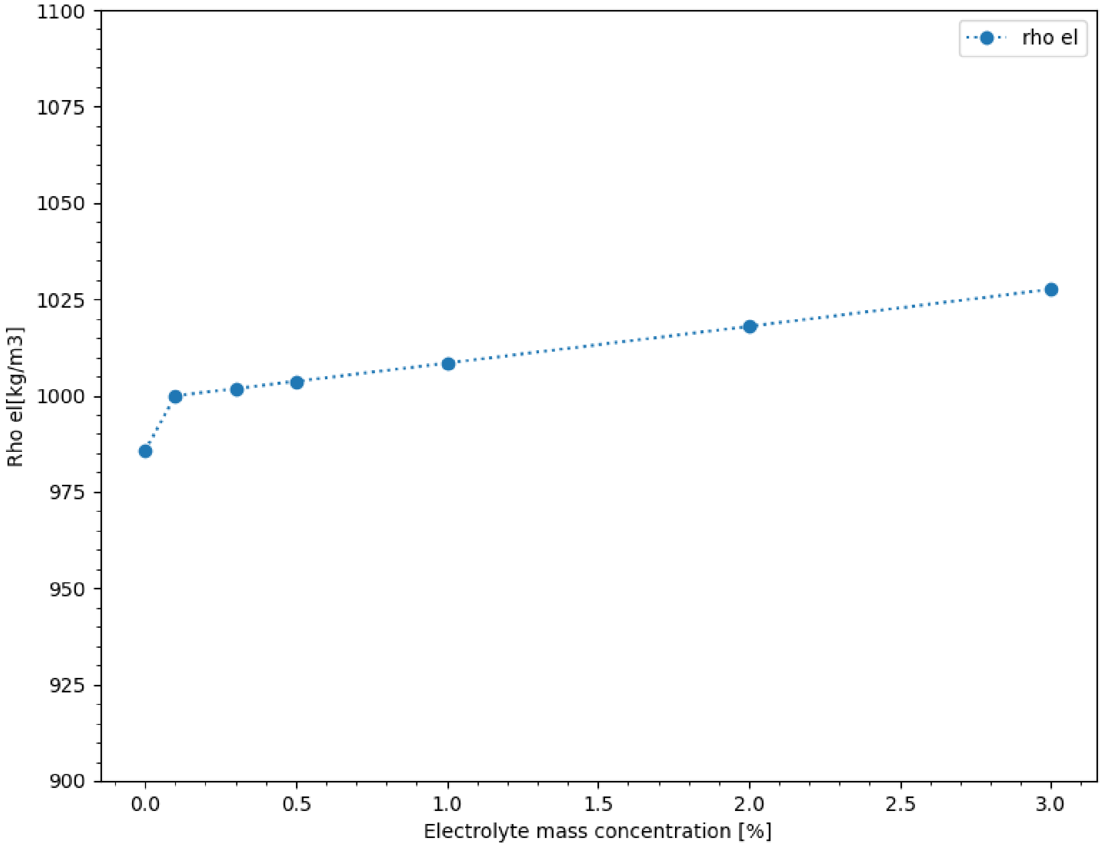


Figure 8: Electrolyte density

For the density is used the Zaytsev correlation: the first point of the concentration at which the density is calculated is the pure water, so it is possible to see the growth of the density at the increasing of the KOH %.

Viscosity

The viscosity of the electrolyte is calculated with the following formula [9] and the results are shown in Figure 10:

$$\mu = exp(K_1 + K_2 * T + K_3 * T^2 + K_4 * Y_i) \quad [16]$$

$K_{1,2,3,4,5}$: constant of the viscosity equation

T: operational temperature in °C (55°C)

Y_i: mass fraction of KOH

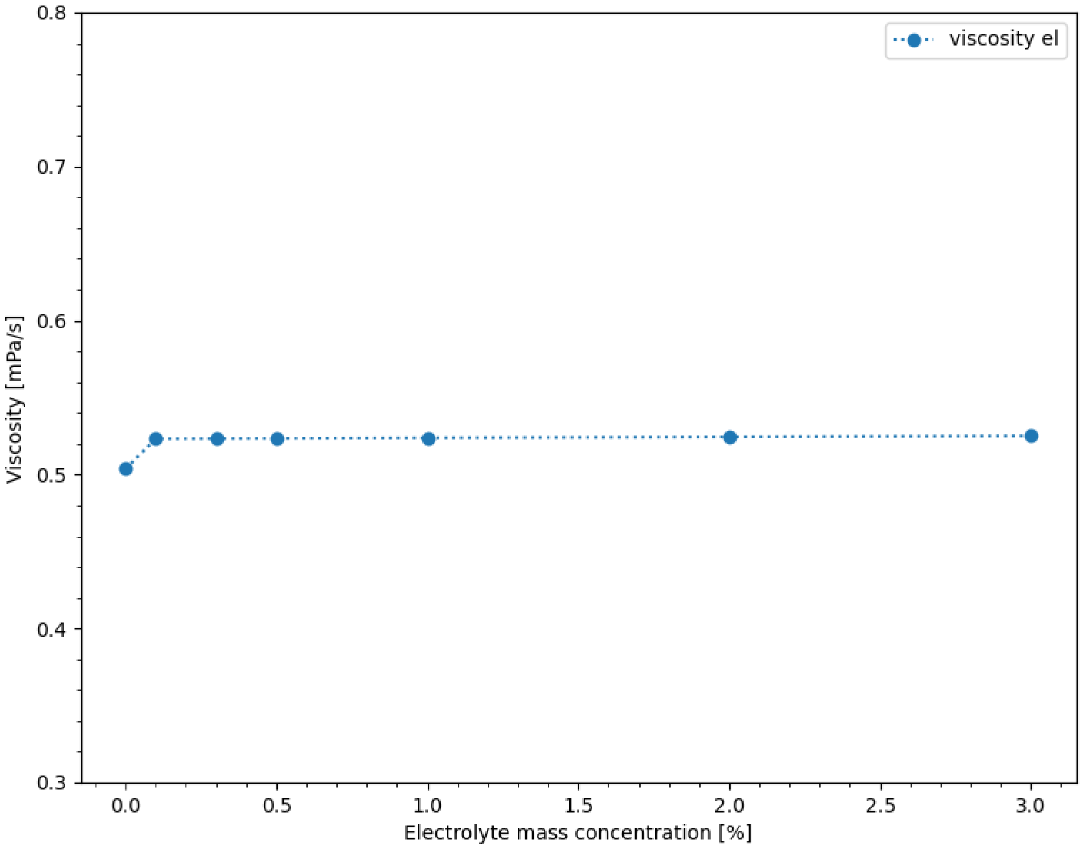


Figure 9: Electrolyte viscosity

For the viscosity was taken the Guo's model: it's possible to see an increment in the viscosity with the growth of the KOH percentage.

Specific heat

The specific heat of the electrolyte is calculated with the following formula [9] and the results are shown in Figure 11:

$$C_p = Y_i * (K_1 * exp(a) + K_5 * Y_i^{K_6}) + (1 - Y_i) * Cp\_water \quad [17]$$

$$\alpha = K_2 * T + K_3 * \exp(0.01 * T) + K_4 * Y_i$$

$K_{1,2,3,4,5,6}$: constant of the specific heat equation

T: operational temperature in °C (55°C)

Y_i: mass fraction of KOH

$C_p$water: specific heat of water [J/kgK]

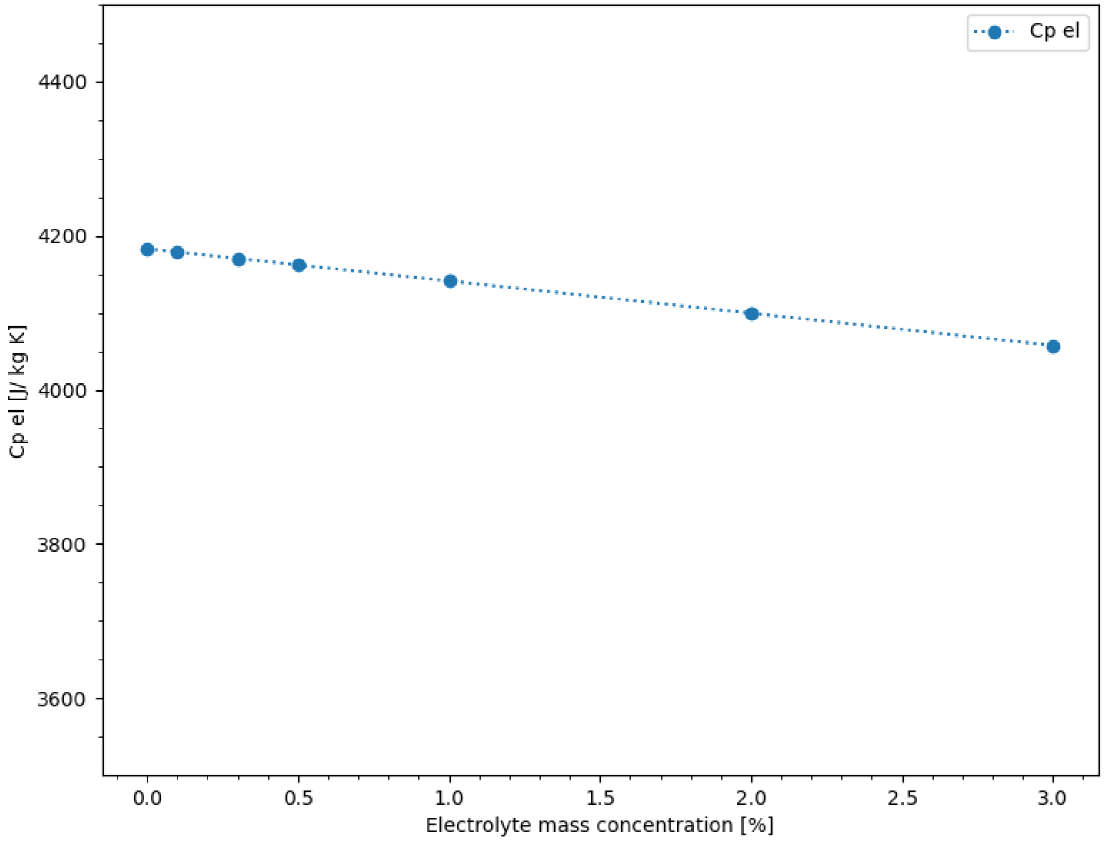


Figure 10: Electrolyte specific heat

It is used the Lalibertée model: the specific heat has a has a downward trend with the growth of the mass percentage of KOH.

Thermal conductivity

The density of the electrolyte is calculated with the following formula [9] and the results are shown in Figure 12:

$$\lambda = (K_1 + K_2 * T - K_3 * T^2) * (1 - Y_i * K_4) \text{ [18]}$$

$K_{1,2,3,4}$: constant of the Thermal conductivity equation

T: temperature in °C (55°C)

Yi: mass fraction of KOH

Cp_{water}: specific heat of water [J/kgK]

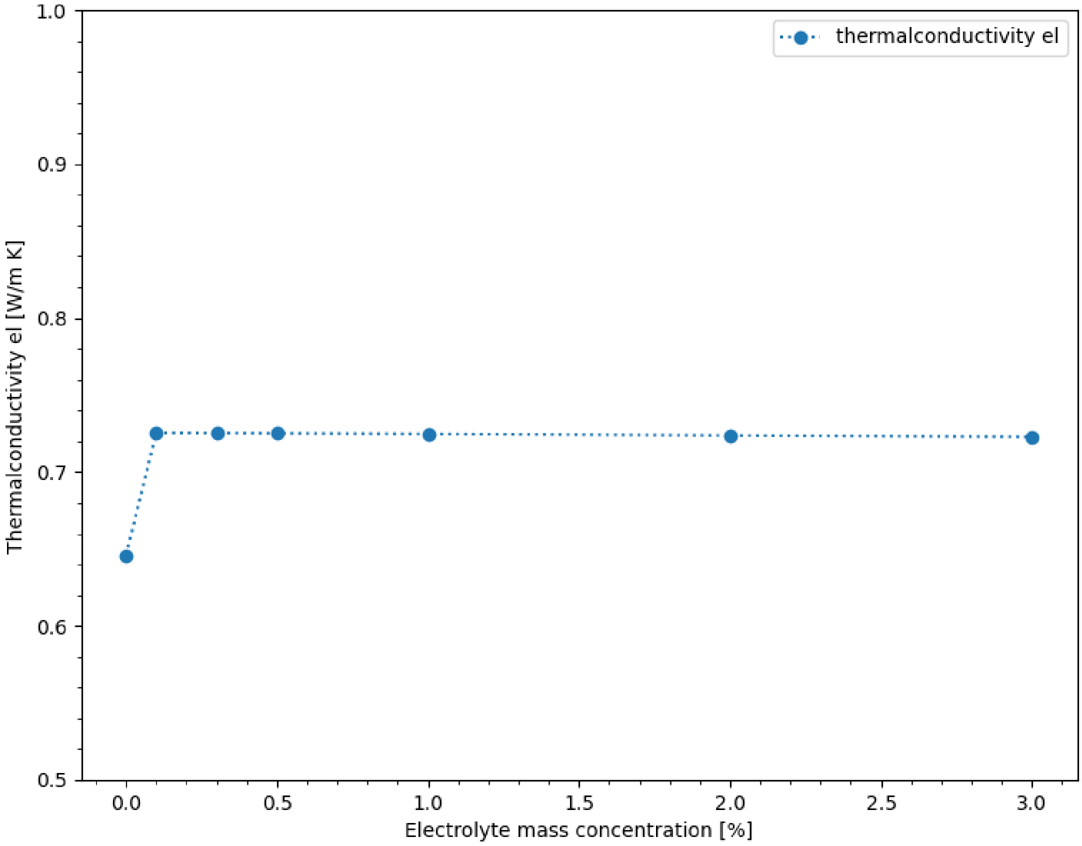


Figure 11: Electrolyte thermal conductivity

The thermal conductivity (that is based on Zaytsev model) of the electrolyte is the term with a big difference compared to the normal water.

3.2 Electrolyte flow

One of the main problems of designing a stack is to understand how much electrolyte is needed. The electrolyte is characterized by a mix of water and usually KOH or NaOH. Other than for the hydrogen production, the electrolyte helps to minimize the heat produced by the electrolysis reaction, maintaining the correct temperature at the reaction site of the MEA [10].

The water flow rate is related to the temperature difference between cell input and output through the dimensionless Lambda factor λ_{H2O}, equal to:

$$\lambda_{H2O} = \frac{2*F}{M_{H2O}*cp_{H2O}*DeltaT}\left(U_{cell} - U_{tn}\right) \text{ [19]}$$

- λ_{H2O} : dimensionless ratio of the water flow rate, just needed for the hydrogen reaction, and to that of the electrolysed water, needed also to dissipate the stack heat
- F: Faraday constant 94486 [C*mol^-1]
- M_{H2O}: molar weight of water
- cp_{H2O}: specific heat of water at constant pressure
- $DeltaT$: temperature difference of water between the outlet and the inlet of the cell
- U_{cell}: voltage of the cell at operational T, p
- U_{tn}: Thermoneutral voltage

Lambda increases with the temperature decreasing and with the increasing of the operational voltage: this is due to the fact it is needed a higher flow rate to maintain the thermal equilibrium in these conditions (Figure 13).

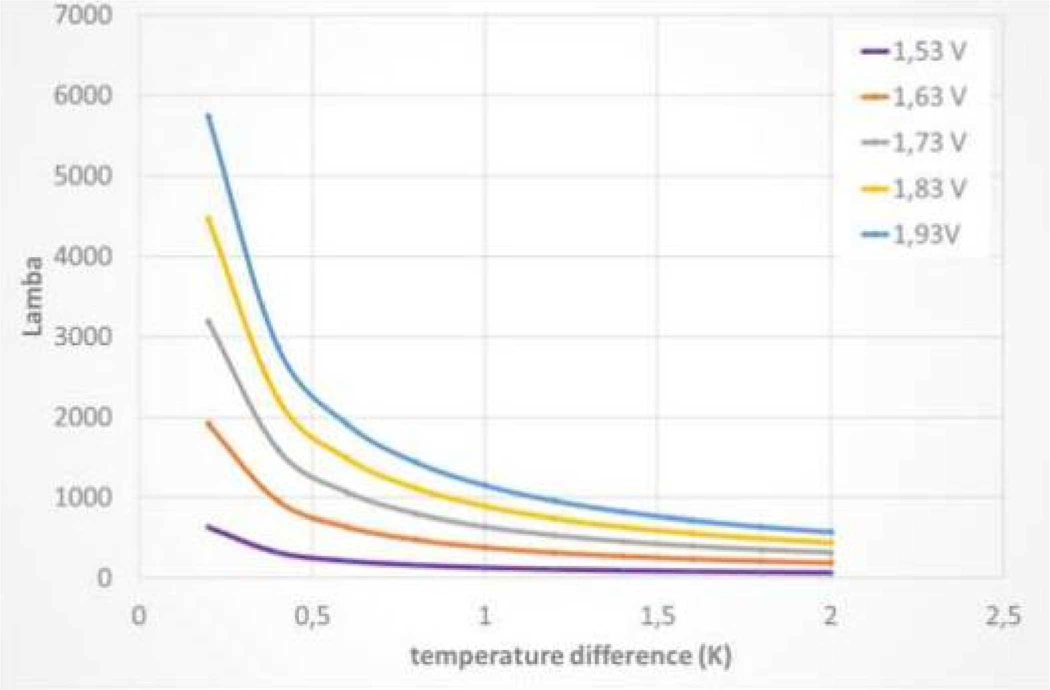


Figure 12: Lambda [10]

To minimize the difference of temperature between the outlet and inlet, another way to determine the flow rate of the inlet water is the utilization factor of water (UF_w). UF_w is the ratio between the water that reacts at a given current and the water that is sent to the anode. The relation between the water flow that reacts, and the current is given by the following formula:

$$n_{H2O} = \frac{i * A * N_{cell}}{z * F} = n_{H2} \qquad [20]$$

- $n_{H2O:}$ water molar flow [mol/s]
- i: current density [A/cm^2]
- A: active area [cm^2]
- N_{cell}: number of cells
- Z: number of ions exchanged during the reaction (in this case is equal to 2)
- F: Faraday's constant [C/mol]

The feed flow rate of water can be expressed in mL/(min^{-1} cm^2) of active area, and the utilization factor can be written as:

$$UF_w = \frac{\left(\frac{i*A*N}{2*F} * MM_{H2O} * 60\right)}{(specific\ feed\ water\ flow\ rate * A * N)} \quad [21]$$

- UF_W: utilization factor [%]
- MM_{H2O}: molar weight of water [g/mol]

It becomes:

$$UF_w = \left(\frac{i*0.0056}{Feed\ water\ flow\ rate}\right) \quad [22]$$

Usually for the AEM technology the UF_w is set equal to 0.5 %. From the graph below, it is possible to see that at higher current densities it is needed a UF_w higher, to minimize the difference of temperature maintaining the reaction rate (Figure 14).

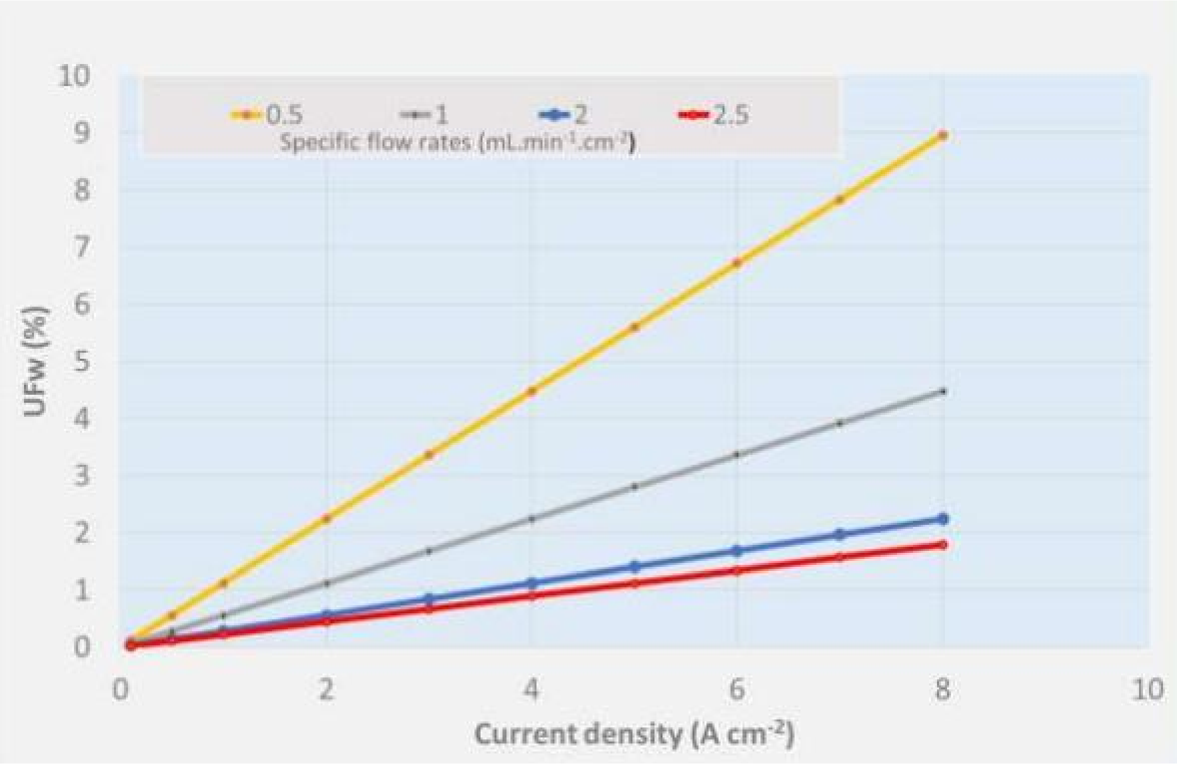


Figure 13: Utilization factor [10]

The water flow, in addition to be a reactant and to help with the minimization of the heat in the electrolysis, it contributes also to the removal of the gas bubble at the elctrodes and their evolution.

For the reason cite above, it’s important to set the inlet water flow rate higher than the minimum one needed for the reaction to form hydrogen and oxygen at given current and active area. Usually for AEM the minimum value of the specific flow rate has to be 2 mL/ (min^{-1} cm^2) of active area.

3.3 Electrolyte tank

The electrolyte tank is where the electrolyte is stored and then sent to the stack. It is linked with two pipes, a forward and a return pipe from the stack, and to one pipe for the rejection of the oxygen from the electrolyte. The quantity of electrolyte (KOH) inside the tank is always the same, it changes just its concentration: during the operational part the water in consumed by the production reaction of hydrogen and so the concentration of the KOH into the water rises. Usually when the tank is full it is 1 wt% but during the operation it can arrive until 3 wt%.

It is very important also selecting the correct material for the tank, that has to resist to the electrolyte properties. With the tank it is important to dimension also the pipes entering and exiting it, in which there will be a constraint on the velocity of the fluid.

3.3.1 Tank sizing

For the tank dimensioning as first thing it is important to know which is the water consumption in the reaction, that is given by:

$$Vol_{H2O} = \frac{i * A * N_{cell}}{z * F} * MM_{H2O} * 3.6 \quad [23]$$

- Vol_{H2O} water consumed during hydrogen reaction [l/s]
- MM_electrolyte: molar weight of the H2O [g/mol]
- 3.6: conversion factor from hour to seconds

Once this value is known, it is possible to choose the number of hours after the refill is wanted. The main parameters to consider selecting the hours of refilling are the following:

- Concentration of KOH: it is recommended to have a value of maximum 3 wt% of KOH in water.
- Temperature: during the refill, depending on how much water is put inside and, on its temperature, the temperature in the tank could decrease in an excessive way. The temperature at which the electrolyte has to go out from the tank is the operational one. So, if it doesn't decrease too much, the thermal power to heat up it could be taken from the excess of power in the stack. But if the temperature in the tank becomes too low (lower than 50 °C), an iter is needed to reach the operational temperature to send the electrolyte in the stack.
- Dimensions: more often the refill is done, lower will be the tank size.

So, knowing the consumption of water during the reaction, selecting several hours after the refilling has to be done it is found the volume of water that has to be refilled:

$$DeltaV = Vol_{H2O} * n_{hour} \quad [24]$$

When the tank is full, as said the percentage of electrolyte is 1%, while it is possible to suppose that when the tank has to be refilled, the concentration has reached 3%. In this way the tank volume is calculated as:

$$V_{tank} = \frac{DeltaV}{(1-\frac{0.01}{0.03})} \quad [25]$$

For what concern the temperature after the refilling, it is simple to define it just doing a simple thermal and mass balance:

$$T_{refill} = \frac{\sum mass*Cp*T}{\sum mass*Cp} \quad [26]$$

The two mass flows that are considering are the electrolyte in the tank and the water that is being filling in the tank. So basically, as more water is put in the tank, as more the risk to have a very low temperature in the tank compared to the operational one. For this reason, the best solution is doing the refill in a shorter period.

3.3.2 Electrolyte pipe

After the dimensioning of the tank, it's the time of the pipe sizing. The pipe that enters and exit from the tank are considered equal, due to the fact the consumption of water and the quantity of oxygen that is sum up to the electrolyte after the stack can be considered as negligible.

So, through a script Python different diameter of LLDPE were analysed from the CheMondis: basing on the quantity of electrolyte that is needed in the stack, a diameter is selected, and a constraint is selected on the velocity into the pipe.

$$Vel_{el} = \frac{Mass_{el}}{3.14*\left(r_{pipe_{in}}\right)^2*rho_{el}} \quad [27]$$

- $Mass_{el}$: mass flow rate of electrolyte [kg/s]
- $r_{pipe_{in}}$: internal ray of the electrolyte pipe [m]
- rho_{el} : density of the electrolyte [kg/m^3]

If the velocity of the electrolyte is higher than 2 m/s, a bigger diameter is selected.

The electrolyte pipes pass into the frame and delivers the fluid at the different cells in the way that is shown in Figure 15: there is a forward pipe, in which the electrolyte is sent from the tank to the anode of the different cells to make the hydrogen formation reaction take place, and a return pipe, in which the fluid used is sent back to the tank and in which, in addition to the fluid, there will also be an amount of oxygen released by the hydrogen reaction.

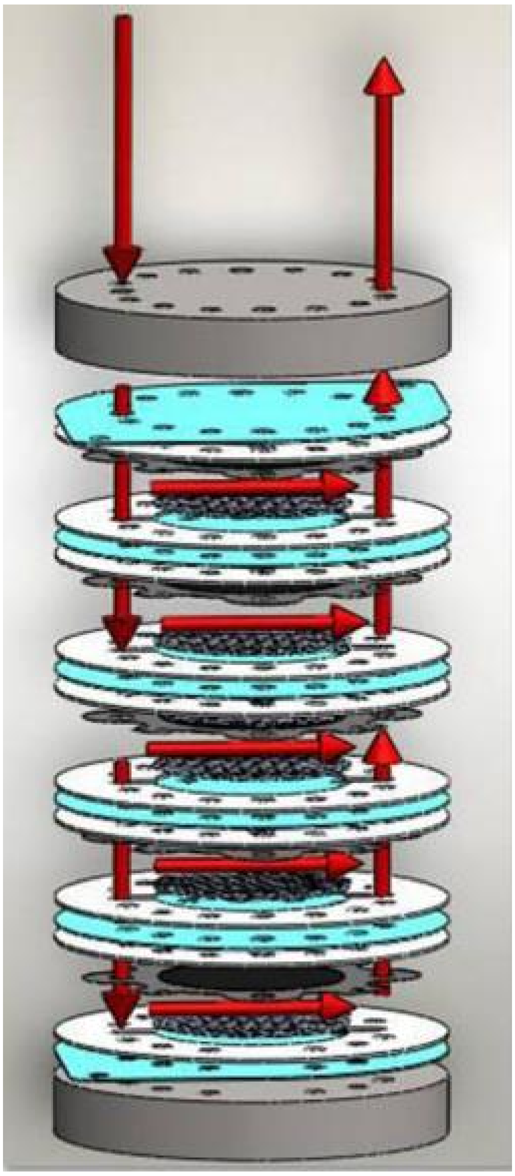


Figure 14: Electrolyte distribution in the stack [11]

4 Air to liquid heat exchanger

The electrolysis process is not an ideal process and due to internal resistances of the cell heat is generated in the stack. So this heat has to be removed, to not damage the components of the stack and the cell itself: a heat exchanger is placed in the circulation cycle [7]. The gases produced are also cooled to condense the water, that can be sent again to the electrolysis system to reduce the water demand. The HE can be located just after the stack or also after the electrolyte tank, to have as fluid just the electrolyte and not a mix of electrolyte and oxygen from the reaction: the mix gas-liquid can damage the heat exchanger. Different applications require different configurations of heat exchangers. In this case has been considered a radiator, using parameters from the Simaco group, that is the supplier for Enapter. The hot fluid is a mix of electrolyte and oxygen, and the cold fluid is air.

4.1 Stack heat losses

As said before, during the electrolysis the stack heats up and this leads to a growth in the electrolyte temperature: so firstly, it is important to know this value. Knowing the power (Q_{stack}) and the efficiency of the stack (eta= 70%) it is possible to calculate the value of heat power that is in excess (Q_{excess}), that is not used. With another assumption, based on the electrolyzer 4.0 of Enapter srl., it is calculated the heat that is losing trough the environment (Q_{env}). Now it is possible to know which is the value of the power that is heating the stack and so the electrolyte flow (Q_{losses}):

$$Q_{excess} = Q_{stack} * (1 - eta) \text{ [28]}$$

$$Q_{env} = 0.3 * Q_{excess} \text{ [29]}$$

$$Q_{losses} = Q_{excess} - Q_{env} \text{ [30]}$$

In this case the HE has been located just after the stack, so the fluid that passes in it is a mix of electrolyte plus oxygen: the properties of the oxygen have been calculated using the Library Cool Prop on Python, while the ones of the electrolyte using the models citated above.

Now the delta temperature that occurs in the stack can be calculated:

$$DeltaT = \frac{Q_{losses}}{(massflow_{el} * c_p)} \text{ [31]}$$

- Massflow_el : mass flow of the electrolyte + oxygen [kg/s]
- Cp: electrolyte + oxygen specific heat transfer at constant pressure

When the mix is heated, after the stack its properties are different and it is needed to recalculate them, at a temperature T= $T_{operational}$ +DeltaT.

4.2 Global Heat transfer coefficient

4.2.1 Hot and cold fluids

In this section it is going to be calculated the global heat coefficient of the mix of electrolyte and oxygen. The diameter of the pipe of the HE will be equal to the one exiting the stack: the latter in turn has been calculated and depends on the quantity of electrolyte is needed for the type of stack.

Once that are known the electrolyte flow and the diameter of the HE pipes, that is equal to the diameter of the electrolyte exiting the stack, it is possible to know the velocity of the fluid inside it:

$$vel_{mix} = \frac{volflow}{3.14*\left(\frac{dpipe_{in}}{2}\right)^{2}} \quad \text{[32]}$$

- Volflow: volumetric flow of the mix in the HE [m^^{3}/s]
- Dpipe_in: internal diameter of the pipe, equal to the pipe exiting the stack [m]

Having the velocity of the fluid inside the pipe and the properties of the fluid the next step is to calculate Reynolds and Prandlt numbers.

$$Prandtl = c_{p_{mix}} * \frac{viscosity}{thermalconductivity} \quad \text{[33]}$$

$$Reynolds = rho_{mix} * v_{mix},* \frac{d_{pipe_{in}}}{viscosity} \quad \text{[34]}$$

These two numbers are dimensionless and are necessary to calculate the number of Nusselt for the electrolyte: the Nusselt number changes its formula based on the value of the Reynold and Prandtl numbers. Considering a smooth pipe of a certain length and subjected to a constant surface temperature, the Nusselt number can be calculated from the following formulas:

$$For\ laminar\ flow: \quad Nu = 3.66 + \frac{0.065*\left(\frac{D}{L}\right)*Reynolds*Prandlt}{1+0.04*\left[\left(\frac{D}{L}\right)*Reynolds*Prandtl\right]^{\frac{2}{3}}}] \quad \text{[35] [12]}$$

$$For\ turbulent\ flow: \quad Nu = 0.023 * Reynolds^{0.8} * Pramdtl^{\frac{1}{3}} \quad \text{[36] [12]}$$

The second equation, known as Cloburn equation and valid for turbulent flow, is valid when [12]:

$$0.7 \leq Prandtl \leq 160$$

$$Reynolds > 10000$$

Once the Nusselt number is calculated, the heat transfer coefficient is:

$$h_{mix} = Nu * \frac{thermalconductivit}{d_{pipe_{in}}} \quad \text{[37]}$$

The same procedure is followed for the air, except that the velocity and the mass flowrate of it are chosen or can be modified during the operations. There could be constraints for the velocity of the air, maybe due to the fan that is chosen. The relations for the calculation of the Nusselt number for the air on the external part of the pipe are the following ones [12] :

$$4 < Reynolds < 40 \quad Nu = 0.911 * Reynold^{0.385} * Prandtl^{0.33} \quad [38]$$

$$40 < Reynolds < 4000 \quad Nu = 0.683 * Reynold^{0.466} * Prandtl^{0.33}$$

$$4000 < Reynolds < 40000 \quad Nu = 0.193 * Reynold^{0.618} * Prandtl^{0.33}$$

$$40000 < Reynolds < 400000 \quad Nu = 0.027 * Reynold^{0.805} * Prandtl^{0.33}$$

The heat transfer coefficient of the air is the following:

$$h_{air} = Nu * \frac{thermalconductivity}{d_{pipe_{out}}} \quad [39]$$

After having calculated the heat transfer coefficients for the air and for the mix, the global heat transfer is given by the following formula:

$$UA = \frac{1}{\frac{1}{h_i A_i} + \frac{1}{h_e A\_e}} \quad [40]$$

- hi,e: heat transfer coefficient of electrolyte and air
- Ai,e : area on which there's exchange of heat, the first i for the electrolyte and the second for the air

4.3 Metodo Ɛ-NTU

This method is used when it is known the exchange surface and the goal is to calculate the thermal power and the outlet temperature of the cold and hot fluids.

Firstly, it is important to define the thermal capacity of the two fluids: the fluid with the lower thermal capacity will suffer the biggest temperature variation and so the maximum variation temperature. The maximum thermal power exchanged in a heat exchanger is:

$$Q\_max = C\_min * (T_h - T_c) \quad [41]$$

- $C_{\_min}$ is the lower thermal capacity between the one of the hot fluids $C_h = Mass_{mix} * Cp_{mix}$, and the one of the cold fluids $C_c = Mass_{air} * Cp_{air}$
- T_h and T_c are respectively the hot and cold temperature at the inlet

Note the maximum thermal power, the efficiency for the HE can be calculated thanks to the number of units of thermal exchange, called NTU:

$$NTU = \frac{UA}{C\_min} \quad [42]$$

- U: global heat transfer coefficient
- A: surface of thermal exchange of the HE
- $C_{\_min}$ lower thermal capacity

The efficiency of the HE can be described in function of the number of units of thermal exchange NTU and of the capacity ratio C ($C_{\_min}/C_{\_max}$). The formula used for the calculation of ε is the one for crossflow, in which both fluids are unmixed.

$$\varepsilon = 1 - exp\,(\frac{NTU^{0.22}}{c}[exp(-c * NTU^{0.78} - 1]) \quad [43]$$

Knowing the efficiency of the HE, the next calculation gives the heat that is exchanged between the cold and the hot fluid:

$$Q_{real} = Q_{max} * \ \varepsilon \quad [44]$$

It is possible to define the temperature in the outlet part for the hot and cold fluid, given by the following formulas:

$$Tout_c = \ Tin_c + \frac{Q_{real}}{C_{air}} \quad [45]$$

$$Tout_h = \ Tin_h - \frac{Q_{real}}{C_{el}} \quad [46]$$

With this method is possible to size the HE, seeing which are the outlet temperature of both fluids. Thanks to this formula, it is possible to calculate the variation of temperature that occurs in the hot and cold fluid.

$$DeltaT_h = Tout_h - Tin_c \quad [47]$$

$$DeltaT_c = Tin_c - Tout_c \quad [48]$$

5 Sizing the stack

5.1 Geometry of the stack

In this chapter it is going to be analysed the structure of the stack, with the definition of the components and the calculations of their dimensions and of their weight. For simplicity the components of the stack that are considered are just the ones that have more impact on the dimensions. For all the components, except for the end plate, is given a fixed thickness that changes among the components.

Cell

It's the heart of the stack. The main components are:

- the anode: it's where the oxidation occurs.
- the cathode: place in which occurs the reduction.
- the membrane: usually is semipermeable and permits to the anions to pass from the anode to the cathode, rejecting gases as oxygen and hydrogen.
- GDL (Gas diffusion layer).

The dimensions of the stack depend mainly on the dimensions of cell: in fact, its active area is the parameter on which depend the areas of the other components, and its thickness multiplied by the number of cells is the parameter with more weight on the length of the stack.

GDLs (Gas diffusion layer)

The GDL is a fibrous porous medium with different functions: it makes happen a distribution of the gases that react on the surface of the electrode and ensure the passage of the electrons from the external circuit. The material of the GDL taken into account for this project is Nickel foam. In a working cell there are two GDLs, one at the cathode and one at the anode: GDL diameters at the cathode and at the anode considered equal among them, with a circular area equal to the active area, but the thicknesses are different and so their volumes are different. This last part will be counted in the calculation of the weight.

$$d_{GDL} = d_{activearea}$$

Bipolar plate

The bipolar plate is the component that separate the reactant gases and distribute them on each side over the whole active area. It separates but also link with the passage of electrons cathode and anodes of different cells. It is made of carbon steel and its diameter is considered equal to the diameter of the active area.

$$d_{bp} = d_{activearea}$$

Insulating cell

The insulating cell is a cell that is between the last cell of the stack and the end plate. Its diameter and thickness are equal to the one of a normal cell, being it equal as a normal cell.

$$d_{ic} = d_{activearea}$$

Frame

The frame enclosures the other components: inside it there are cells, GDLs, bipolar plates and the pipes where the electrolyte and the hydrogen pass. The material used is PPS GF40; the frame can be considered as a ring and so the inner diameter is equal to the diameter of the active area, while the external diameter linearly depends on the size of the electrolyte pipes. In the frame are present also the screws, that keep close the stack.

$$d_{frameout} = d_{activearea} + 2 * d_{pipe_{el}} + 4 * t \quad [49]$$

- $d_{pipe_{el}}$: is the diamater of the electrolyte pipe. In the formula is multiplied by two because in the frame pass two pipes, one for the inlet flow and one for the outlet
- t: is the thickness that has to be left for security between the electrolyte pipe and the inner and outlet boarder of the frame.

End plate

The end plate (there's one cathodic and one anodic) is the component that keep the structure compact, applying a pressure on the cells to avoid the gas escaping between the plates. The material used is the INOX 316L, and its the diameter is considered 2 cm larger than the frame diameter.

$$d_{ep} = d_{frameout} + 2 \quad [50]$$

As regard the thickness instead, for this component it is calculated: the thickness of the end plate has to resist to the stresses that occurs on it.

$$endplate_{thickness} = ((3 * (5 + v) * (1 - v)) * \frac{pressure*(d_{endp})^4}{(16*E_p*Spost_{centro})^{1/3}} \quad [51]$$

- E_p : 20000 [Mpa]
- d_{endp}: diameter of the endplate [m]
- $v = 0{,}3$
- $pressure : is\ the\ atmospheric\ pressure, equal\ to\ 0.1\ MPa$
- $Spost_{centro}$ = 0.1

5.1.1 Calculation of the stack length

The length of the stack is the sum of al the components that have been analysed in this chapter. The GDL thickness is counted in the cell thickness. The length of the stack is given by the following formula:

$$Stack_{lenght} = Cell_{thickness} * N_{cell} + 2 * endplate_{thickness} + 2 * insulatingcell_{thickness} \quad [52]$$

The parameter that influences more the length of the stack is the first one, which is formed by number of the cells multiplied by the number of cells in the stack.

5.1.2 Calculation of the weight

Once the geometrical part is calculated, the next step is the calculation of the weight of the stack. Knowing the area of each component and their thicknesses, it’ possible to calculate the volume of each. The area of GDL, of the upper and lower end plate, of the bipolar plate are calculated using the following formula, it just changes the diameter in the different situations:

$$Vol = 3.14 * \left(\frac{d}{2}\right)^2 * thickness \quad [53]$$

For what concern the frame the situation is quite different because the frame can be considered as a ring, and so the formula becomes:

$$Vol_{frame} = 3.14 * \left(\frac{(d_{frame_{out}} + d_{frame_{in}})}{2}\right) * \left(\frac{(d_{frame_{out}} - d_{frame_{in}})}{2}\right) * thickness_{frame} \quad [54]$$

The thickness of the frame is equal to the one of the cells, while the diameters one is the inner one and the other the more extern.

Multiplying the volume for the densities of the materials it’s possible to know the mass of each component. The mass of the complete working cell is the following one:

$$wc = 2 * mass_{GDL} + mass_{frame} \quad [55]$$

In a working cell there are two GDLs, one at the cathode and one at the anode, and for this reason the mass is multiplied by two. The mass of the cathode, anode and membrane can be considered as negligible.

The weight of the stack (without screws) can be considered as one part variable and one part fixed.

$$Fixed = uep + lep + 2 * ic + ec24 * 2 \quad [56]$$

- Uep: upper end plate weight
- Lep: lower end plate weight
- Ic: insulating cell weight
- Ec24: bipolar plate weight

As said before, in the stack there are two endplates (one up and one low), two insulating cells between the two last cells and the endplate, and two bipolar plates.

$$Variable = Ncell * wc + (Ncell - 2) * ec24 \quad [57]$$

- Ncell: number of cells in the stack
- Wc: weight of the working cell
- Bp: weight of bipolar weight

The total weight of the stack, without considering the screws, is given by the following formula:

$$Totweight = Fixed + Variable \quad [58]$$

6 Screws

Defining the dimension of the stack is essential talking about the way the stack in enclose. The stack taken in consideration is kept closed with pull rods, washers, and nuts. The purpose is to calculate the forces acting on the screws to select the number of these latters for the assembling of the stack, to guarantee the correct sealing during the work. The length of the screws is considered equal to the length of the stack.

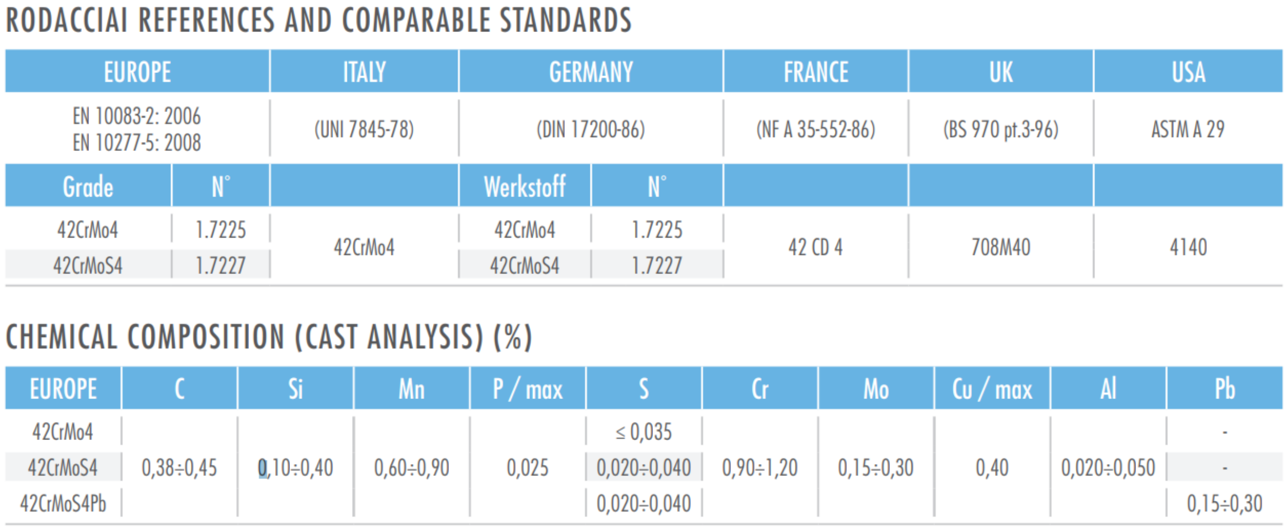
6.1 Screws introduction

In the next table some properties of the screw are shown (Table 1):

Screw details	Symbol	Value	U.M.	Notes
Material		RK1		42CrMo4 - see datasheet
Class of resistance		10,9		
Allowable stress	$R_{p0,2}$	770	MPa	from datasheet
Min. screw diameter	D_{min}	7,1	mm	
Min. resistance screw section	A_t	39,57185	mm^2	
Elongation %	Δ	8		from datasheet

Table 3: Screw properties

The material that is considered is tempered steel, according to the 10,9 class of resistance (UNI EN ISO 898-1:2013), but for prototypes the supplier use RK1 – 42CrMo4 steel. In the table below are shown the properties of the material, taken from Rodacciai datasheet (Table1, Table 2):



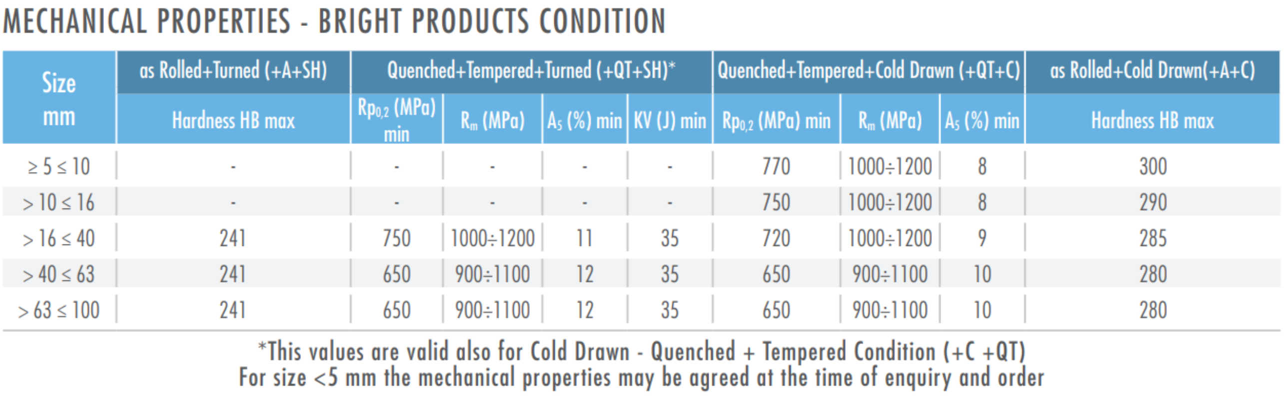
RODACCIAI REFERENCES AND COMPARABLE STANDARDS

EUROPE		ITALY	GERMANY		FRANCE	UK	USA
EN 10083-2: 2006 EN 10277-5: 2008		(UNI 7845-78)	(DIN 17200-86)		(NF A 35-552-86)	(BS 970 pt.3-96)	ASTM A 29
Grade	N°		Werkstoff	N°			
42CrMo4	1.7225	42CrMo4	42CrMo4	1.7225	42 CD 4	708M40	4140
42CrMoS4	1.7227		42CrMoS4	1.7227			

CHEMICAL COMPOSITION (CAST ANALYSIS) (%)

EUROPE	C	Si	Mn	P / max	S	Cr	Mo	Cu / max	Al	Pb
42CrMo4	0,38÷0,45	0,10÷0,40	0,60÷0,90	0,025	≤ 0,035	0,90÷1,20	0,15÷0,30	0,40	0,020÷0,050	-
42CrMoS4					0,020÷0,040					-
42CrMoS4Pb					0,020÷0,040					0,15÷0,30

Table 4: Rodacciai datasheet [17]



MECHANICAL PROPERTIES - BRIGHT PRODUCTS CONDITION

Size mm	as Rolled+Turned (+A+SH)	Quenched+Tempered+Turned (+QT+SH)*				Quenched+Tempered+Cold Drawn (+QT+C)			as Rolled+Cold Drawn(+A+C)
	Hardness HB max	$R_{p0,2}$ (MPa) min	R_m (MPa)	A_5 (%) min	KV (J) min	$R_{p0,2}$ (MPa) min	R_m (MPa)	A_5 (%) min	Hardness HB max
≥ 5 ≤ 10	-	-	-	-	-	770	1000÷1200	8	300
> 10 ≤ 16	-	-	-	-	-	750	1000÷1200	8	290
> 16 ≤ 40	241	750	1000÷1200	11	35	720	1000÷1200	9	285
> 40 ≤ 63	241	650	900÷1100	12	35	650	900÷1100	10	280
> 63 ≤ 100	241	650	900÷1100	12	35	650	900÷1100	10	280

*This values are valid also for Cold Drawn - Quenched + Tempered Condition (+C +QT)
For size <5 mm the mechanical properties may be agreed at the time of enquiry and order

Table 5: Rodacciai datasheet [17]

For the calculations the allowable stress is considered equal to $R_{p0,2}$ = 770 [MPa] [17].

The number of screws that can keep the stack joined can be calculated with the next formula:

$$n_{viti} = \left(\frac{d_{frameout}}{40}\right) + 4 \qquad [\,59\,]$$

- dframeout: is the diameter of the frame

The maximum force that can be applied on a screw has not to overcome the value of the maximum allowable stress:

$$F_i = K * A_t * S_p \qquad [\,60\,]$$

- A_t is the resistant section of the thread or the minimum value of the diameter of the screw.

- S_p the value of the limit tension = $R_{p0,2}$ allowable stress
- K is a parameter between 0,75-1. For statical application is 0,85.

6.2 Forces evaluation

The forces that act on a screw are mainly the following ones:

- Forces depending on the stack assembly (F_a);
- Forces due the internal operative pressure (F_p);

From the Enapter data, it's possible to consider a total closing momentum (M_t) of 19 [Nm] applied on each screw, so with the next formula is calculated the force due to the assembly of the stack:

$$M_t = 0{,}2 * F_a * d \quad [61]$$

- d is the nominal diameter of the screw [m].

The forces due to internal operative pressure (F_p) are calculated as follow: firstly, is considered a operational nominal pressure and it is selected a security coefficient (1.5), so for the test the pressure at the worst scenario is equal to the multiplication between them. This pressure is acting on a circular area, on a diameter smaller than the frame (3 cm smaller). It is found a force value for this area, that divided by the screws gives the force acting on a single screw.

6.2.1 Verifications

The total axial force applied on the screws is the sum of the two contribute:

$$F_{tot} = F_a + F_p \quad [62]$$

It has to be lower than the total force that can withstand,

$$\frac{F_i}{F_{tot}} \cong 1{,}3 \quad [63]$$

This security coefficient can be selected among the one in the Table 3, 4, 5. In absence of shocks and vibrations and with a low frequency, z can be selected equal between 1-1.5. For this reason, it has been selected equal to 1.3.

If the relation between $F_i \text{ and } Ftot$ is not respected, it's possible to add a pair of screws, keeping the same class of resistance, and recalculate the forces that act on the stack (it could be just one screw, but having a circular area on which put the screws is better always add an even number of screws).

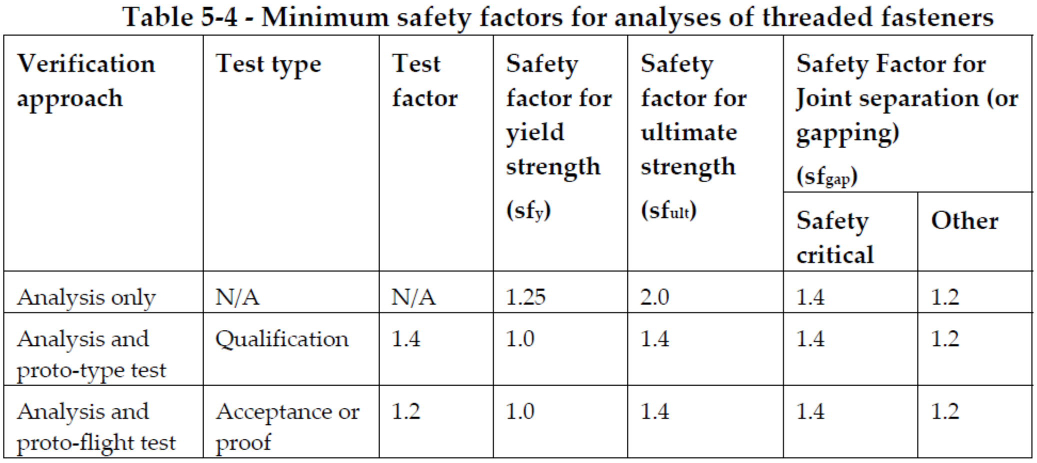


Table 5-4 - Minimum safety factors for analyses of threaded fasteners

Verification approach	Test type	Test factor	Safety factor for yield strength (sf_y)	Safety factor for ultimate strength (sf_{ult})	Safety Factor for Joint separation (or gapping) (sf_{gap})	
					Safety critical	Other
Analysis only	N/A	N/A	1.25	2.0	1.4	1.2
Analysis and proto-type test	Qualification	1.4	1.0	1.4	1.4	1.2
Analysis and proto-flight test	Acceptance or proof	1.2	1.0	1.4	1.4	1.2

Table 6: Safety factors [18]

6.3 Calculation of the screws weight

Knowing the number of screws, it's now possible to calculate the mass their total mass. The volume of a single screw was calculated using a medium radius between the maximum and the minimum one and multiplying this value for the density of the material, it is possible to know the mas of the screw.

$$Mass_{screw} = density * \left(\frac{d_{medium}}{2}\right)^2 * 3.14 * screwlenght \quad [64]$$

- density: is the density of the RK1 – 42CrMo4 steel
- screw length: is the length of the screw, equal to the length of the stack

The total mass of the screw is given by the mass of the single screw and the number of screws that are needed in the stack.

6.4 Calculation of the stack weight

Now that also the mass of the screws has been calculated, the weight of the stack is given by:

$$Totweightstack = fixed\ weight + varibale\ weight + Nscrews * mass_{screw} \quad [65]$$

Once it is known the total weight of the stack and so all the weights of the single components, it's interesting to have a look how the weight varies with the number of the cell and the percentage influence of each component on the total weight. These calculations are done fixing the power of the stack, the current density, the voltage of the cell and varying the active area of the cell, that also determines the number of the cells that are required to provide that power.

7 Power supply unit

The PSU is one of the most important components of an electrolyzer: it is necessary to give power to the stack. The PSU has different requirements to meet:

- it must have enough power to cope with the load.
- In the compact design of Enapter has to resist to high temperature, like 50 degrees. If the temperature is high, the efficiency of the PSU can drop dramatically.
- voltage or current have to be adjustable: the purpose is to impose one of them and then the stack defines the other one. The production of H_2 can be considered linearly dependent with the current.
- it has to respect the Enapter constraints: it has to be compact and produced in series.

To know some models that can be interesting for the application, a market analysis was carried out: products from the Mean Well and XPpower firms. The Mean Well produces a PSU of about 3200 W, one of 5000 W and the other one for Mean Well has 10000 W of power. the acronym for the first one is DOU, while for the other two RST. For future applications and with a higher power, the company XPpower was contacted. (acronym HD or HP). Its PSUs reach up to 5000W and there's the possibility to put the devices in parallel, reaching 25 KW of power. There's a difference between the product at 3 KW and at 5 KW and it's that the input changes: for the lower one the input is single phase, while for the one with the higher power is tree-phase. From the point of view of regulation, three-phase is better regulated even if several machines are connected, while the same cannot be said for single-phase, since overlapping can lead to harmonics that are harmful to the system. In addition, the PSU can be controlled either remotely via an internal data bus or analogue. When the voltage exceeds its limit value, there is a self-regulation that brings the value back into the range.

To select the correct PSU an optimization should be done, based on the cost/Watt, the dimensions and the current and voltage in output (Table 5).

Modello	*Power[W]*	*Cost[€]*	*€/W*	*Nominal DC Voltage [V]*	*Current range [A]*
HDL3000PS60	*3000*	*800*	*0,27*	*60*	*0-50*
HDS3000PS60	*3000*	*800*	*0,27*	*60*	*0-50*
DOU_3200_48	*3216*	*523,2*	*0,16*	*48*	*0-67*
HPD4K5TS075	*4500*	*800*	*0,18*	*150*	*0-31,5*
RST_5000_48	*5000*	*1200*	*0,24*	*48*	*0-105*
HPL5K0 series	*5000*	*800*	*0,16*	*200*	*0-25*

HPT5K0-L series	*5000*	*800*	*0,16*	*200*	*25*
RST_10000_48	*10000*	*1920*	*0,19*	*48*	*0-210*

Table 7: PSU cost

In the next graph the ratio cost per power is shown (Figure 16):

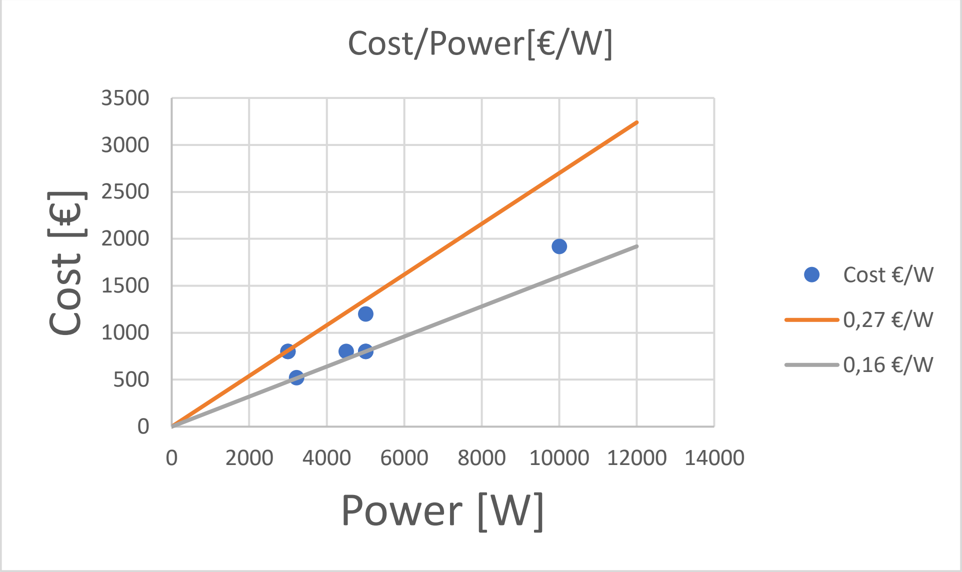


Figure 15: PSU cost/W

As is possible to see from the graph, the cost per power is usually lower at higher powers of the PSU, except for the model RST_10000_36.

8 Cost of the raw material

This model calculates the waste in euro of the materials in the AEM package, which must be cut from sheets sent by suppliers. Sheets are sent in different formats and with different costs, and the lowest possible material waste cost must be found. This model can then be applied to different materials in the AEM package.

8.1 Model

To calculate the discarded material cost and thus make an optimisation, we must first define the active area of the electrolytic cell: this area is the size of the raw material we need.

First, however, we go on to define the size of the sheets from which we will cut and obtain the raw material in the desired dimensions. These measurements are taken, as mentioned above, by the company's suppliers. In developing the model, fictitious costs and dimensions are used, but congruent with what might happen:

- F1: Area= 0.992 m^2, price= 50 €/m^2
- F2: Area= 0.249 m^2, price= 200 €/m^2
- F3: Area= 0.062 m^2, price= 500 €/m^2

The electrolytic cell that has been considered has a circular shape, and this is equal to the diameter of the active area. So, the diameter is derived from the following formula:

$$d_{raw\ material} = \sqrt{A_{active} * 4/\pi} \quad [66]$$

The cutting of the raw materials from the sheet is done in the company and is not done exactly on the diameter of the active area, but a safety edge must be left in order not to damage the raw material: this edge was selected equal to 5 mm.

$$d_{plus} = d_{raw\ material} + edge \quad [67]$$

The next step is calculating the number of raw materials that can be cut from the sheet. But to do that, considering that the sheet is rectangular, it's considered a quadratic area around the raw material:

$$A_{quad} = d_{plus}^2 \quad [68]$$

The diameter of this area is the diameter of the active area plus the edge.

Now the numbers of raw materials that can be contained in a sheet and can thus be cut is provided by the following formula:

$$N_{raw\ material} = \frac{Area_{sheet}}{A_{quad}} \quad [69]$$

- $Area_{sheet}$: rectangular area of the sheet where the raw material have to be cut.

The number of the raw material of mea ~~s~~heet, if it is a value with the comma, is approximated to the lower value.

This is the quadratic area big as the diameter plus, and it will be needed to calculate the discarded.

Once it is known the number of raw materials which is possible to cut and the quadratic area, it is possible to calculate the discarded of the sheet:

$$discarded = A_{sheet} - A_{plus} * N_{raw\ material} + \left(A_{quad} - A_{plus}\right) * N_{raw\ material} \quad [\ 70\ ]$$

- $A_{quad} - A_{plus}$: is the difference between the square and the circular area around the raw material

Now, knowing the cost of the different sheets and the values of the discarded materials, it is possible to know which is the cost of the discarded sheets in the different configurations:

$$cost_{discarded} = discarded * cost_{sheet} \quad [\ 71]$$

8.2 Calculations

As said, the goal is to calculate the cost of the discarded area of the raw material of the mea sheets. For each sheet (F1, F2, F3) are going to be analysed different sizes of the area of the raw material, to see which is the best solution in terms of cost per discarded area. The dimensions of the areas considered area are the following ones: 50, 70, 80, 100, 150 and 200 cm^2.

The number of pieces that is possible to obtained changes with the dimension of the active area: higher is this value, less numbers are obtained. Having the number is then calculated the discarded area, which is later multiplied by the cost of the sheet.

The results of the calculations are the following ones, where the discarded area cost is in % respect to the total cost of the sheet (Figure 17):

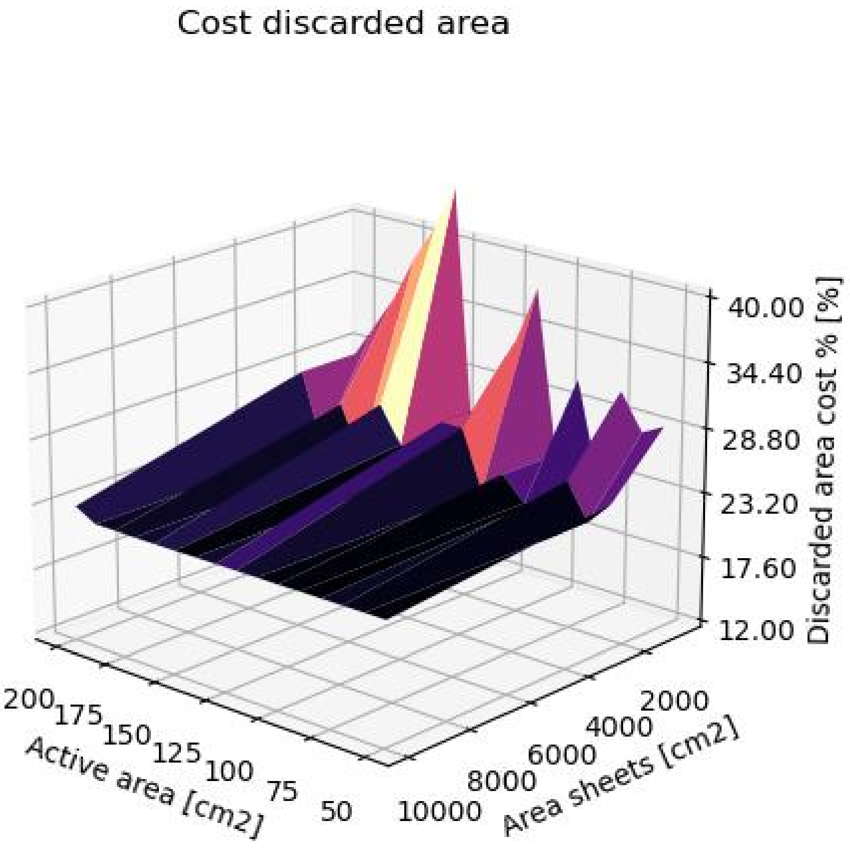


Figure 16:Cost of the discarded area

As possible to see from the graph, the maximum discarded area cost in percentage respect to the total cost of the sheet is when the area of the sheet is low: this is since smaller is the sheet and more is expensive. Then also the raw material of the mea, also if they're small, are more expensive if they're cut from the smallest sheet, being it the most expensive one (Figure 18).

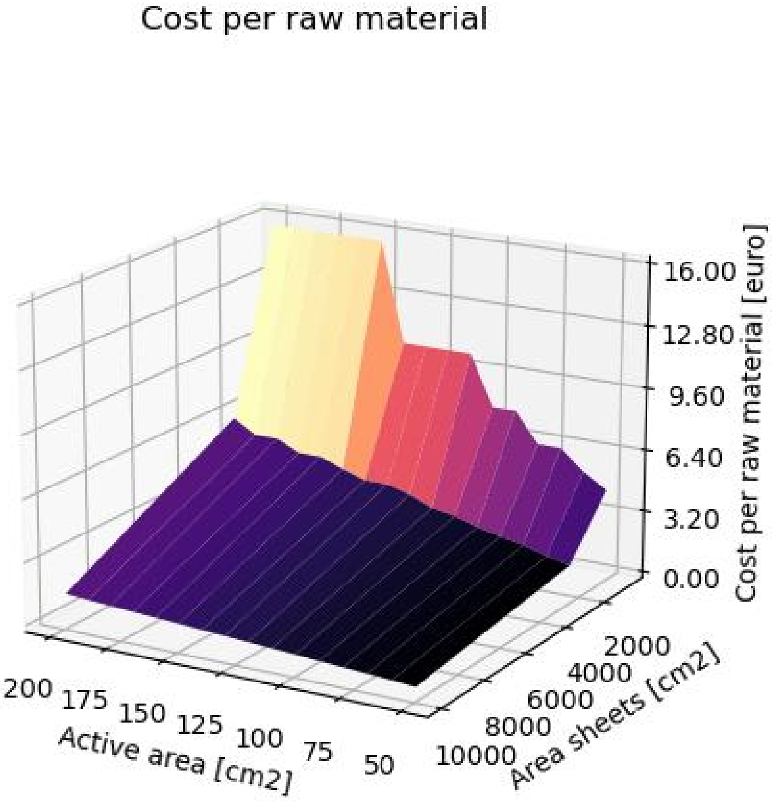


Figure 17:Cost per high value material

Having a look on the results, the raw material and the discarded cost per raw material are lower when the sheets are bigger and especially when they have a lower prize.

9 Dimensions calculations

The main point of this part is to determine the sizes of the stack and compare other output parameters, like the production of hydrogen, changing the power of the stack and the active area of the cell. The results are obtained with a Python script.

9.1 Description

As said before, in this section there's the study of the stack components and parameters that changes with the variation of the stack power and of the active area. The powers of the stack that have been imposed are equal to 25000 W, 50000 W and 500000W and the values of the area instead were chosen equal to: 50, 70, 80, 100, 150 and 200 cm^^{2}. This value was chosen to see how the outputs of the study change with the variation of these inputs' parameters.

Other input parameters are considered constant:

- Operational temperature, which remains equal to 55 °C;
- Operational pressure, equal to 30° bar;
- Current density ($i_{density}$);
- Voltage of the cell (U_{cell}), that depends on the operational temperature and on the current density, that are constant.

In the next part of this chapter are going to be analysed the parameters that are affected by the stack power and active area changes.

9.2 Current

The first parameter that is calculated is the current: its value is directly proportional to the change in the active area of cells. As more the area is bigger, as more the value of the current that flows in the stack is higher.

$$I = i_{density} * Area_{active} \quad [72]$$

- $i_{density}$: current density [A/cm^^{2}]
- $Area_{active}$: active area of a single cell[cm^^{2}]

However, not all current values can be considered valid: in fact, when choosing the power supply unit (PSU), it must be checked that it can support the current demand of the stack.

9.3 Number and voltage of the cell

The cell is the heart of the stack, where the hydrogen reaction takes place. The number of the cell depends both on power and active area:

$$N_{cell} = \frac{W_{stack}}{i_{density} * Area_{active} * U\_cell} \text{ [73]}$$

If the result gives a value with the comma, the number is approximated to the upper integer value. Results are shown in Figure 19.

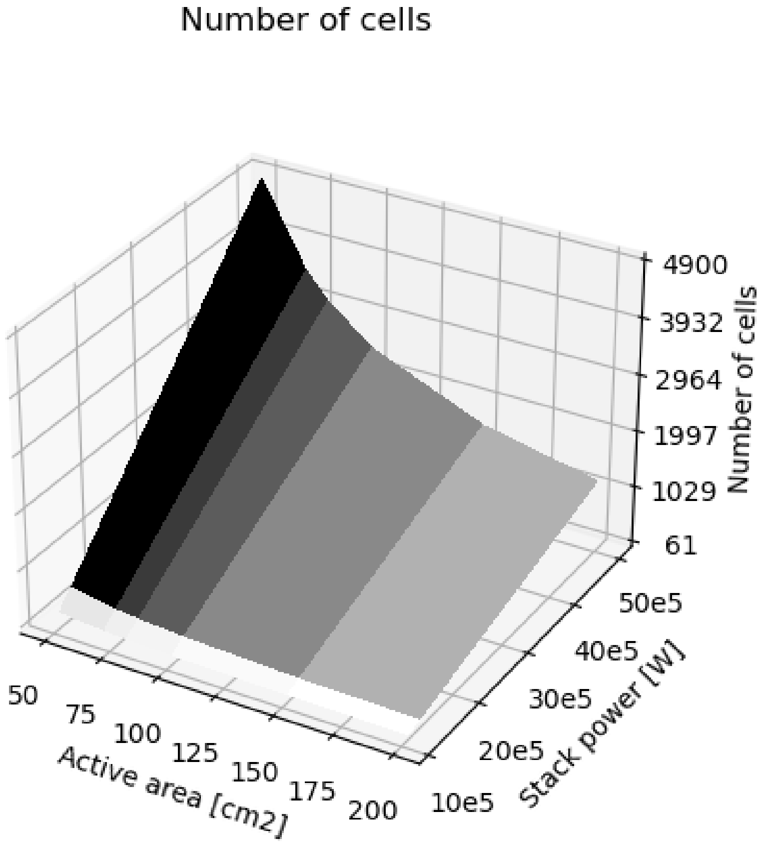


Figure 18:Number of cells

From the table, it is possible to see that, with a fixed power and changing the active area, the number of cells become lower at bigger areas, while with at fixed area and increasing the power, the number of cells grows.

The voltage of the stack is directly proportional to the number of cells: higher is the number, higher is the voltage that is needed.

$$U_{stack} = U_{cell} * N_{cell} \text{ [74]}$$

For this parameter, as for the current, it is important to have a look at it for the choose of the PSU.

9.4 Electrolyte

9.4.1 Quantity of electrolyte needed

Knowing the quantity of hydrogen produced, it is possible to calculate the minimum quantity of water that is needed for the reaction and using the utilization factor UF from formula 22 it's possible to calculate the quantity of electrolyte sent into the machine (Figure 20). It doesn't consider the quantity of fluid which helps dissipate heat in the stack.

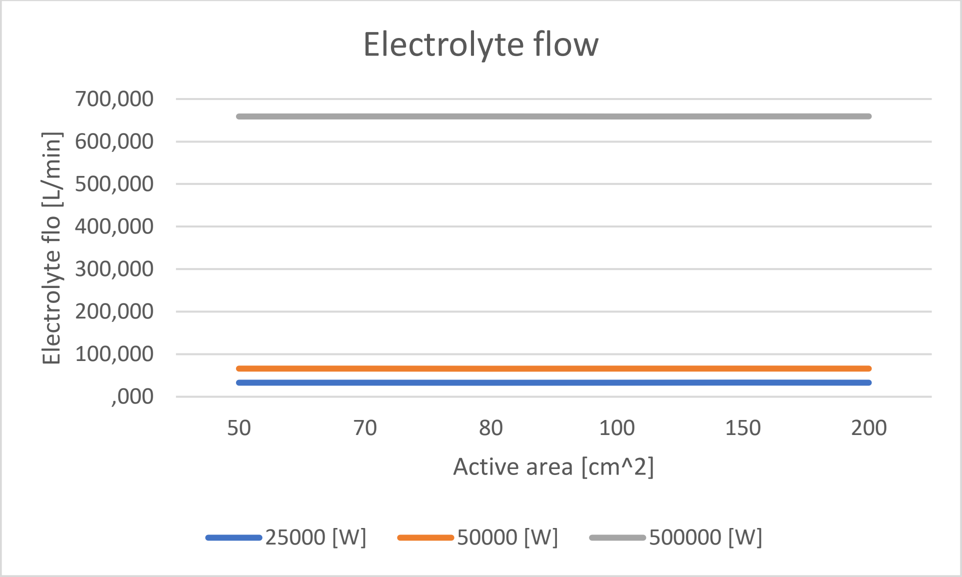


Figure 19: Electrolyte flow

How it's possible to see, the quantity of electrolyte remains constant at a fixed power: this is since it depends mainly on the current density, which for this study is considered constant, and on the water consumed in the reaction for producing hydrogen. That is why the value of electrolyte flow is constant for a certain power, varying only the active area.

9.4.2 Electrolyte pipe in the stack and water tank

The quantity of electrolyte defines the dimension of the pipes that bring the electrolyte in the stack: using the formula 27 with the only constraint of imposing a top speed of the fluid into the pipe of 2 m/s, it's possible calculate the diameter of the pipe that passes through the stack and through all the components. The pipes so are constant at every power, also changing the area, due to the fact they depend only on the quantity of electrolyte that passes inside.

Being constant at every power the quantity of electrolyte and the diameter of the pipe, another parameter that remains constant at every power is the tank [Table 6]: at a fixed time of refilling, the volume that has to be refilled is dependent on the water consumed by the hydrogen reaction, that changes just changing the power.

	50 [cm^2]	70 [cm^2]	80 [cm^2]	100 [cm^2]	150 [cm^2]	200 [cm^2]
25000 [W]	5.06	5.05	5.04	5.06	5.10	5.06
50000[W]	10.10	10.10	10.09	10.12	10.14	10.12
500000 [W]	100.82	100.83	100.83	100.82	100.84	100.86

Table 8: Volume Tank [L]

9.5 Stack length and weight

9.5.1 Length

As said in the previous chapter, the stack length is directly proportional to the number of cells of the stack. The thicknesses of the different components (working cell, GDL, bipolar plate) is considered constant, while only the end plates change: this is due to the presence of the diameter of the end plate inside the formula of the end plate thickness(formula 5), which is equal to the frame diameter and varies with the active area dimension: as more this latter dimension is higher, as more the thickness is bigger, to be able to resist to bigger stresses. The length of the stack varies as in Figure 21:

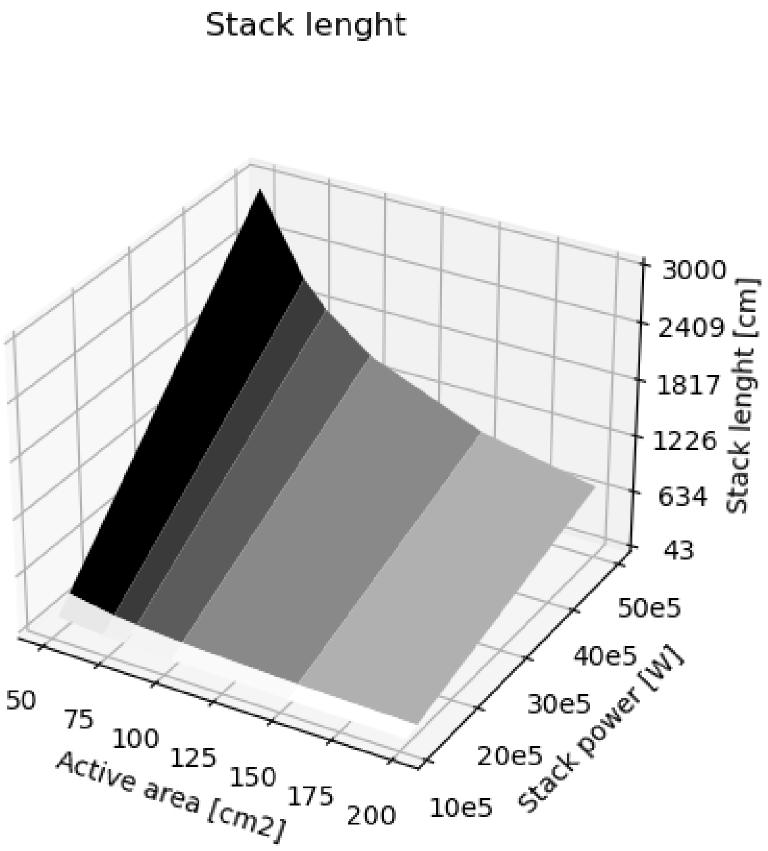


Figure 20: Stack lenght

From the figure it is possible to see that the length of the stack is smaller when active area is bigger, and so when the number of cells is lower.

9.5.2 Screws

The number of screws needed for the stack were calculated using the model explained in the chapter on screws 6.1, where a strength class (the 10.9) was considered. The results are shown in the following table (Table 7):

	50 [cm^2]	70 [cm^2]	80 [cm^2]	100 [cm^2]	150 [cm^2]	200 [cm^2]
25000 [W]	10	12	12	12	14	14
50000[W]	10	12	12	12	14	14
500000 [W]	18	18	18	20	22	24

Table 9: Screws number

As can be seen, the number of screws is greater when the surface area of the active area is larger, and therefore all other components also have a larger area, because the diameter where the pressure acts is larger and therefore there are greater forces to counteract.

9.5.3 Weight

The weight of the stack depends on a fixed weight, on a variable weight and o the number of the screws that must be installed to keep everything together.

From the calculation of the Python script, the weight of the stack has the same behaviour of the length of the stack: it is smaller when the active area is bigger (Figure 22).

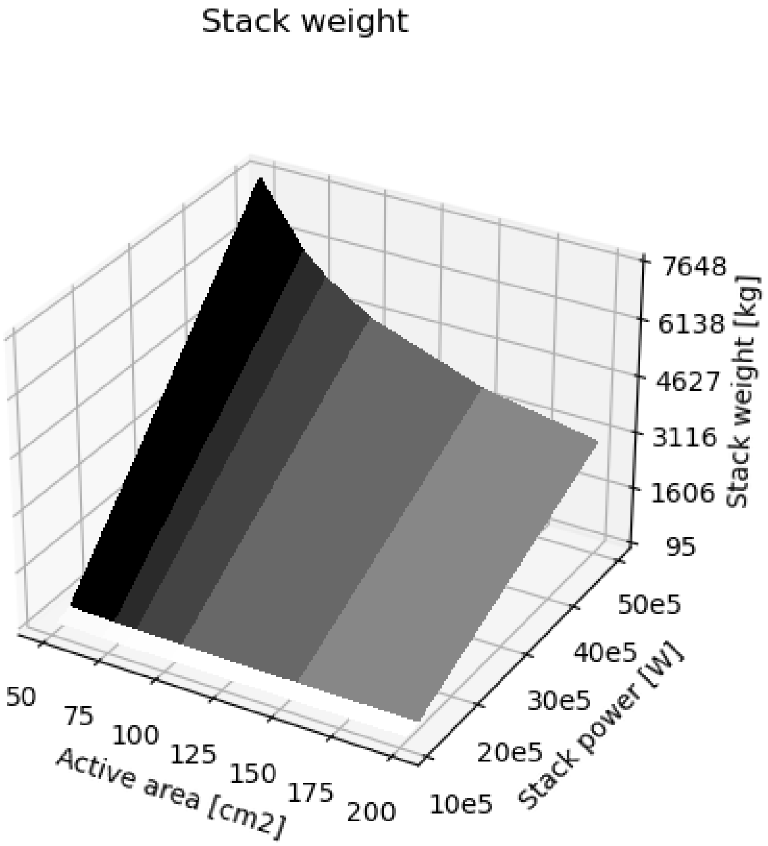


Figure 21:Stack weight

This can be explained by analysing the weight of the different components and their percentage on the total weight of the stack. This study has been done fixing a power of the stack and just varying the area of the active cell; the value of the stack power was chosen equal to Enapter value, to have the confirm if the results are correct or not.

The weight of the stack varies depending on the active area and consequently on the number of cells: bigger is the active area, a smaller number of cells are needed. In the following graph are shown the percentages of all the components, respect to the total weight of the stack (Figure 23):

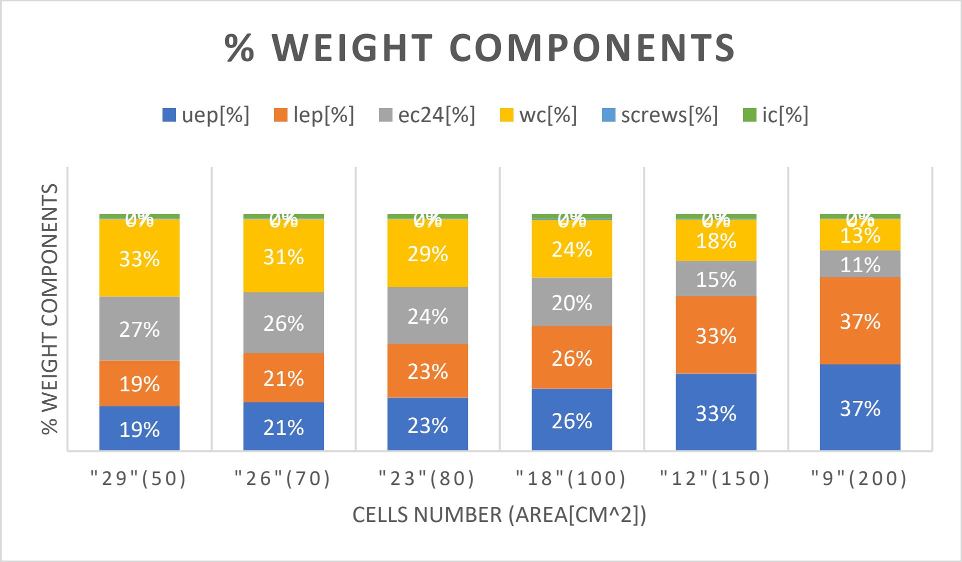


Figure 22: % Weight components at a fixed power, equal to Enapter one

The acronyms of the components of the graph are the following ones:

- uep: upper endplate weight
- Lep: lower end plate weight
- Ic: insulating cell weight
- Ec24: bipolar plate weight
- Screws: weight of the screws

At lower values of the active area and so high values of cells number, the working cell is the principal component also in terms of weight. But when the active area grows the end plates are the heaviest components and this can be explained just seeing the chapter 5.1: the thickness of the endplate is proportional to the diameter of this latter, and so when the diameter of the active are grows, the diameter of the endplate grows and so its thickness. If the diameter and the thickness are bigger, this means that the component is heavier. The screws, as it's possible to imagine, are the lightest component.

In the next figure (Figure 24) in the below part are shown the weights of the different components, and the total weight of the stack is depicted in brown (TOT):

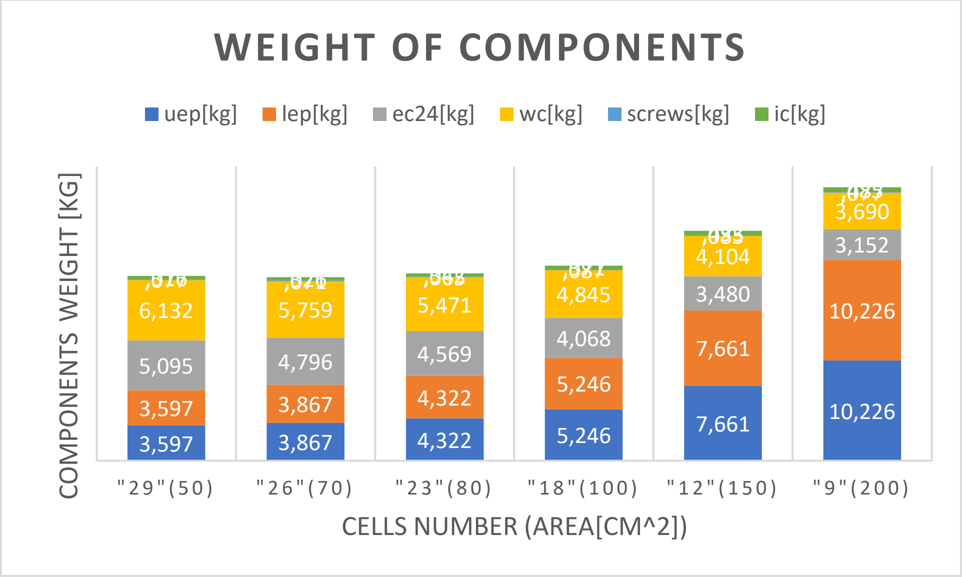


Figure 23: Weight of components at a fixed power, equal to Enapter one

From the weight of components graph it' possible to notice what it was being saying before: when the active are smaller and the number of cells high, the working cell is the heavier parameters, but this changes when the active area grows and the number of cells become smaller, where the end plates are the heaviest components.

9.6 Calculations Heat Exchanger

The main goal for this part is to size the heat exchanger for different powers, changing the temperature of the air and the length of the entire coil of the HE. The model used to obtain the following results is the NTU heat exchanger dimensioning model. The type of radiators studied and considered to define possible proportion coefficients comes from the company Simaco.

9.6.1 Methodology

Firstly, the powers considered and studied are the same as those used in the other chapters of the thesis and are equal to 25000, 50000 and 500000 W respectively. As seen before, the amount of electrolyte for a given stack power does not change as the active area of a single cell changes, as the total area of the stack remains constant. The amount of electrolyte in the stack circuit varies only as the power varies: for this reason, an active area of the single cell equal to 50 cm^2 was chosen.

Other prameters are:

- Operational temperature T= 55°C
- Operational pressure p=30 bar
- Current density
- Number of cells: 23
- Voltage of the cell: 2.4[V]
- The properties of the electrolyte are calculated using the formulas of chapter 3.1, while the ones for the oxygen using Coolprop.

The quantities that vary are the temperature of the air being sent into the heat exchanger and the total length of the HE coils. To calculate the heat exchange area of the radiator and the air flow area, coefficients based on Simaco radiators were used to correlate these two with the total length of the coil.

9.6.2 Hot fluid side (electrolyte and oxygen)

Knowing these functional parameters and using the electrolyte model explained in chapter 2, one can calculate the amount of hydrogen produced, the water consumed during the reaction, and by means of the utilisation factor (formula 22) obtain the amount of electrolyte to be sent to the stack. The diameter of the tube through which the electrolyte passes has already been dimensioned (chapter 3.3.3) and is equal to the diameter of the heat exchanger.

The temperature change of the electrolyte as it passes through the stack is given by the following relationship (formula 23): this is directly proportional to the power loss of the stack and inversely proportional to the electrolyte flow rate in the tube and the specific heat. The latter, the temperature of operation being constant for all different powers, does not vary. The electrolyte flow rate varies linearly with power since it is directly related to hydrogen production, and therefore the temperature delta is the same for each power of the stack.

So, the electrolyte temperature after the stack is given by the formula 31.

Beyond the stack, however, there is not only the electrolyte but also the oxygen produced at the anode: compared to the electrolyte, its mass percentage is very small, but was nevertheless considered for the calculation of the properties. These were calculated at the temperature this mix has after the stack: the properties of the oxygen were calculated using Coolprop, while those of the electrolyte using the formulas in the chapter 3.1.

Then, using the mass percentages of oxygen and electrolyte, the percentages of the mix leaving the stack and entering the heat exchanger the properties are obtained:

$$Property_{mix} = \sum Mass\_percentage\ (Electrolyte, oxygen) * Property\ (Electrolyte, oxygen) \quad [75]$$

Knowing the quantity of the mix passing through the tube, the diameter of the tube and the temperature at which the mix enters the exchanger, the Prandtl and Reynolds numbers are calculated: the heat transfer coefficient is then derived using the formulas 39.

9.6.3 Cold fluid side (air)

The cold fluid used to cool the electrolyte is air. For the dimensioning of the heat exchanger, different temperatures were taken at which air is sent into the exchanger, to simulate operation in different geographical areas. The temperatures analysed are: 5, 10, 15, 20, 30, 40 °C.

In a first moment the air speed was set firstly at 15 m/s, having analysed several Simaco radiator. The cross area, on the other hand, was calculated by means of coefficients relating the length of the pipe and the air passage area. Knowing the latter, the air flow rate sent into the heat exchanger can be calculated.

The properties of the air for the heat exchanger part are calculated at an average temperature between that of the air and that of the surface where the heat exchange takes place (per simplicity this latter is taken as the average temperature between the inlet and outlet of the hot fluid):

$$T_{mean} = \frac{(T_{air} + (\frac{Th_{in} + Th_{out}}{2}))}{2} \quad [\,76\,]$$

By then calculating the Prandtl and Reynolds numbers, the thermal exchange coefficient for air is obtained with the formula 40.

Then, following the e-NTU method explained in the chapter above 4.3, the exchanged heat and the outlet temperature for the hot and cold fluid are calculated.

In a second step, a pipe length of the heat exchanger was set, whereby a heat exchange area of the fins was found by means of the different coefficients. By fixing this, it was desired to see how the delta of temperatures of the hot fluid changes as the air velocity of the fan changes, also analysing the Reynolds numbers. In addition, the case where the electrolyser is at an altitude of 2000 metres was analysed: the pressure at which the air is different from the one analysed before, while the environmental temperature range remains the same. To calculate the new density is use the formula of the gases:

$$rho_{air} = \frac{P_{air} * rho_o * T_o}{P_o * T_{air}} \quad [\,77\,]$$

- Rho_{air}= density of the air at 2000 meters [kg/m^3]
- P_{air}= pressure of the air at 2000 meters [Pa], equal to 79500 [Pa]
- T_{air}= ambient temperature at 2000 meters [K]
- P_o, T_o, rho_o= pressure, temperature and density at standard conditions

In this way it is possible to calculate the new density and consequently see how the Reynolds number varies and so the heat transfer coefficient. From this latter depends how much the hot fluid temperature changes.

9.6.4 Results

Once you have all the results, you can proceed with analysing them. As mentioned, the goal is to size with the best solution a heat exchanger for different stack powers and air temperatures. A total coil length is then assigned to each power, which is obtained with Simaco coefficients and with which the total heat exchange area, fin area and air cross area can be calculated

The best design conditions of the heat exchanger were then identified for each power stack. To show the results, only the 25000 W case has been reported, as working with proportional coefficients would simply double the size of the 50000 W case.

The optimisation of the dimensions was mainly based on the temperature variation of the hot fluid: the temperature variation of the electrolyte inside the stack for any power, as indicated by the formula 31, remains constant and equal to 1.9 °C. This means that, as can be seen from the graph (Figure 20), the conditions for this temperature difference to be bridged within the HE and for the fluid not to cool too much are that the DeltaT is between 1.8-2 °C. Using the temperature variation that the fluid must have as a reference; you can see the area of the fins and then the total length of the coil is needed. The temperature variation of the hot fluid is shown in Figure 20:

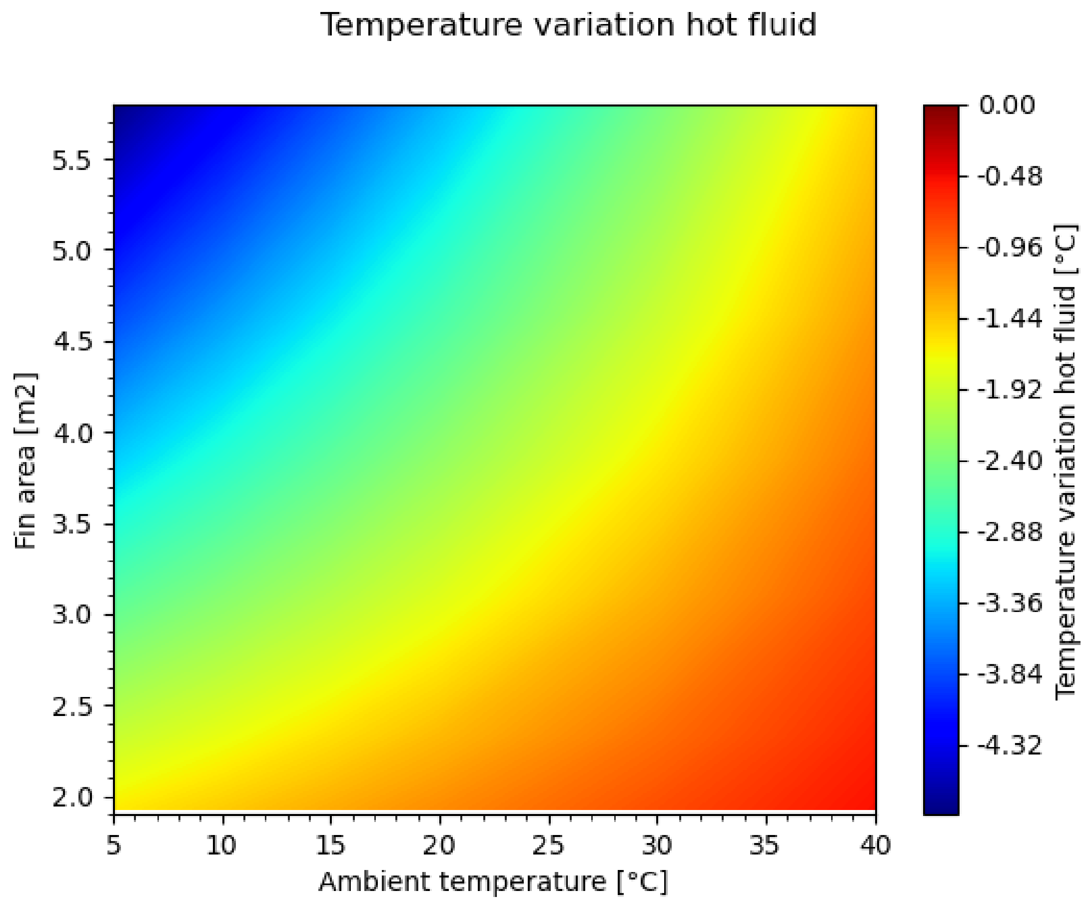


Figure 24: Temperature variation of the hot fluid

From the graph, the temperature delta is greatest when the air temperature in the room and the size of the fin area are smallest: this is since heat exchanged takes place over a smaller surface area and the temperature difference between the fluids is greatest. The air velocity was considered constant considering Simaco's parameters.

The lower figure (Figure 21) shows the power exchanged between the two fluid considering variable air temperature and fin area:

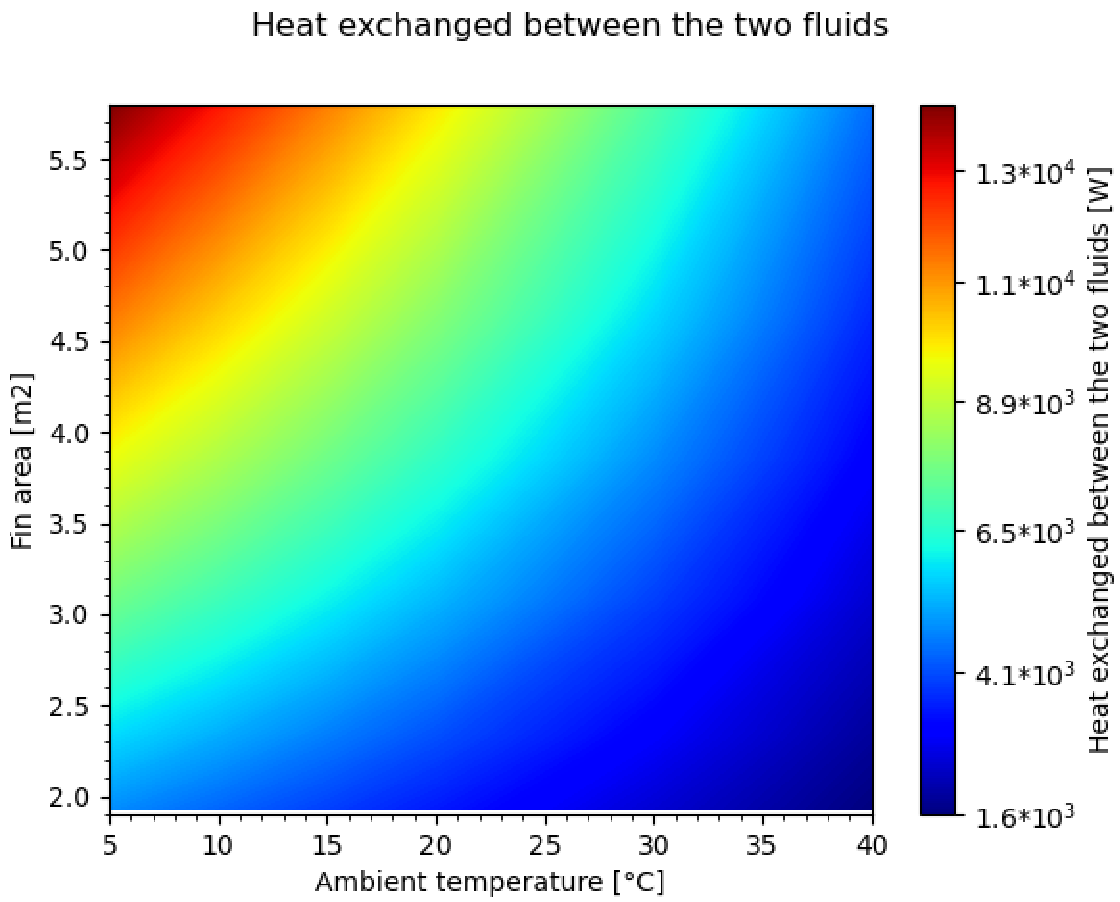


Figure 25: Heat exchanged between the fluids

Here, the maximum values of power exchanged between fluids occur when the air temperature is lowest, and the fin area is highest: in this case the air that is needed to cool down the hot fluid would have an higher delta temperature.

After dimensioning the heat exchanger, an area of the fin was chosen: thus, it was studied how the temperature of the hot fluid varies with air velocity and ambient temperature (Figure 27).

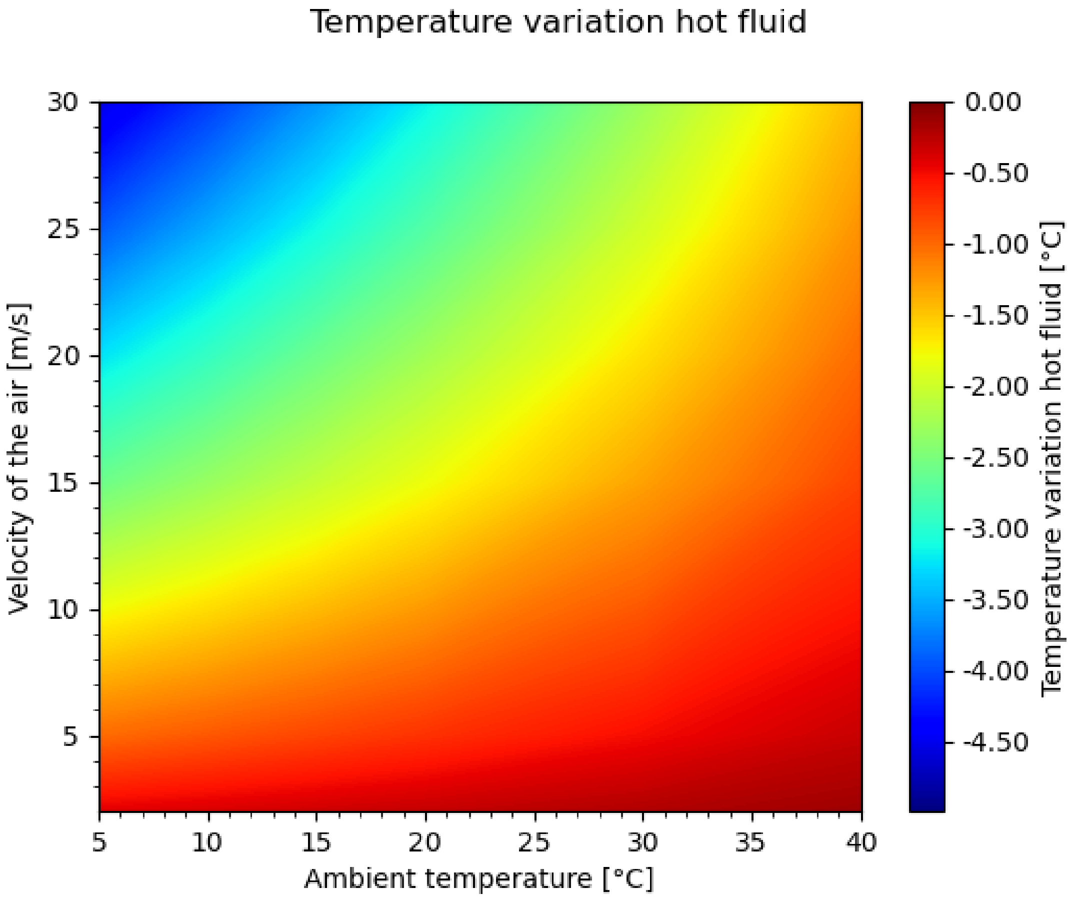


Figure 26: Temperature variation hot fluid at fixed fin area

It can be seen from the figure that there is a greater decrease in the temperature of the hot fluid when the air velocity is higher, and its temperature is lower. In Figure 28 instead, it represents how the Reynolds number varies.

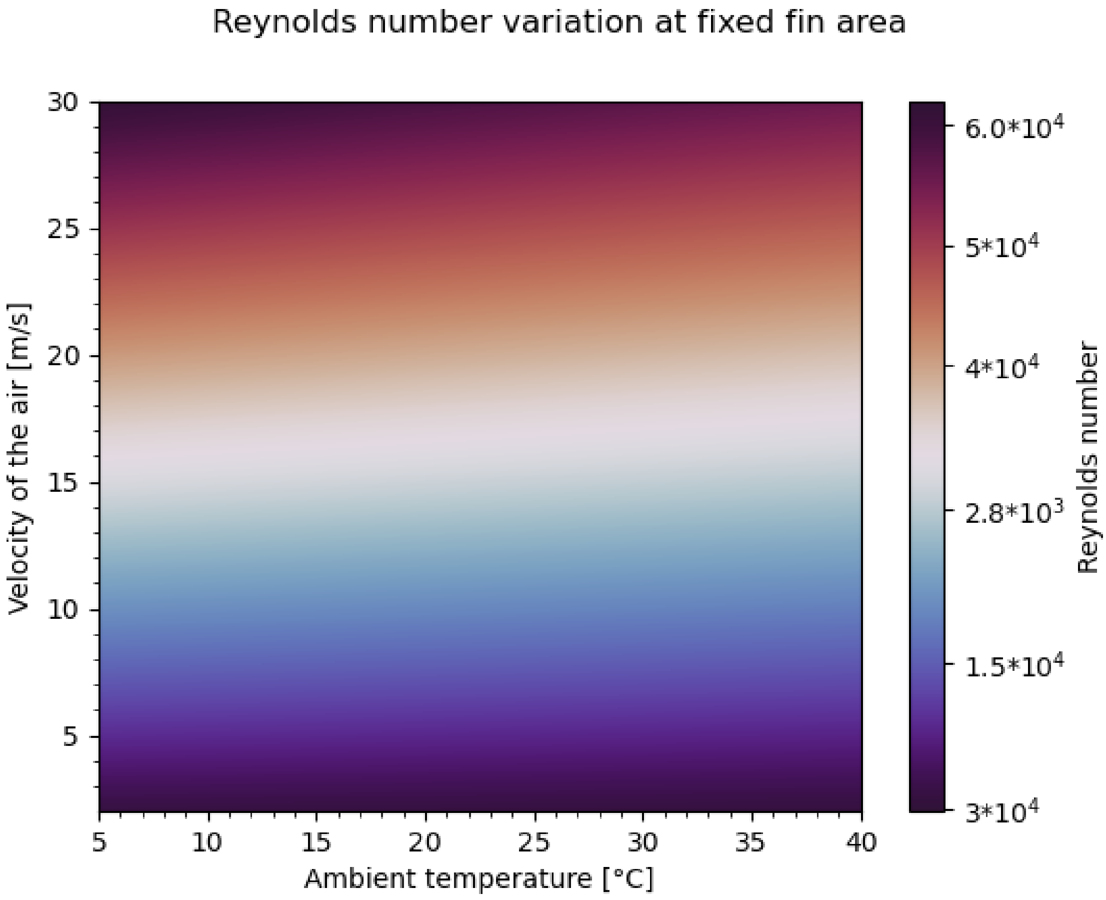


Figure 27: Reynolds variation of air

The case where the electrolyser is at an altitude of about 2000 metres above sea level is analysed next. As mentioned earlier, knowing the pressure at that altitude, the density of the air at that altitude can be calculated using the gas equation (formula 63): as the altitude increases, it decreases, causing the Reynolds (Figure 29) and consequently the heat transfer coefficient to decrease. This causes the hot fluid to have a smaller temperature variation (Figures 30).

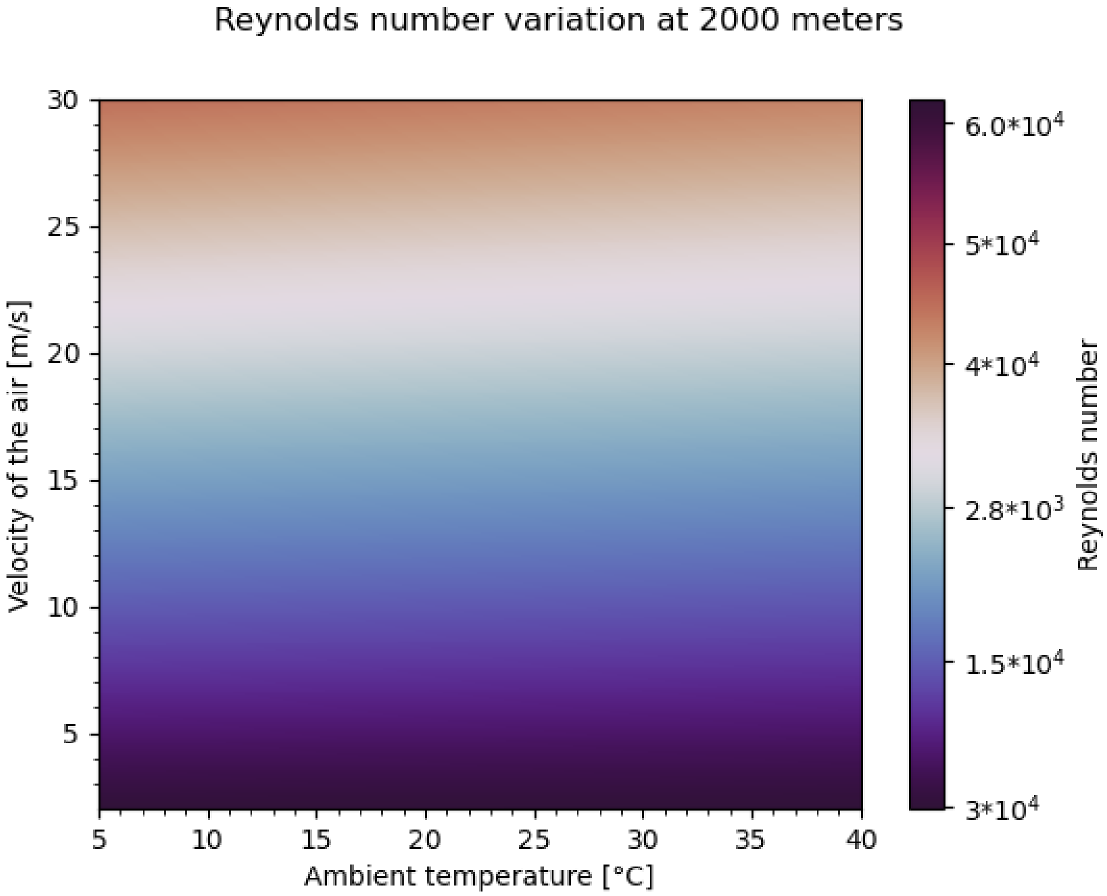


Figure 28: Reynolds variation at 2000 meters

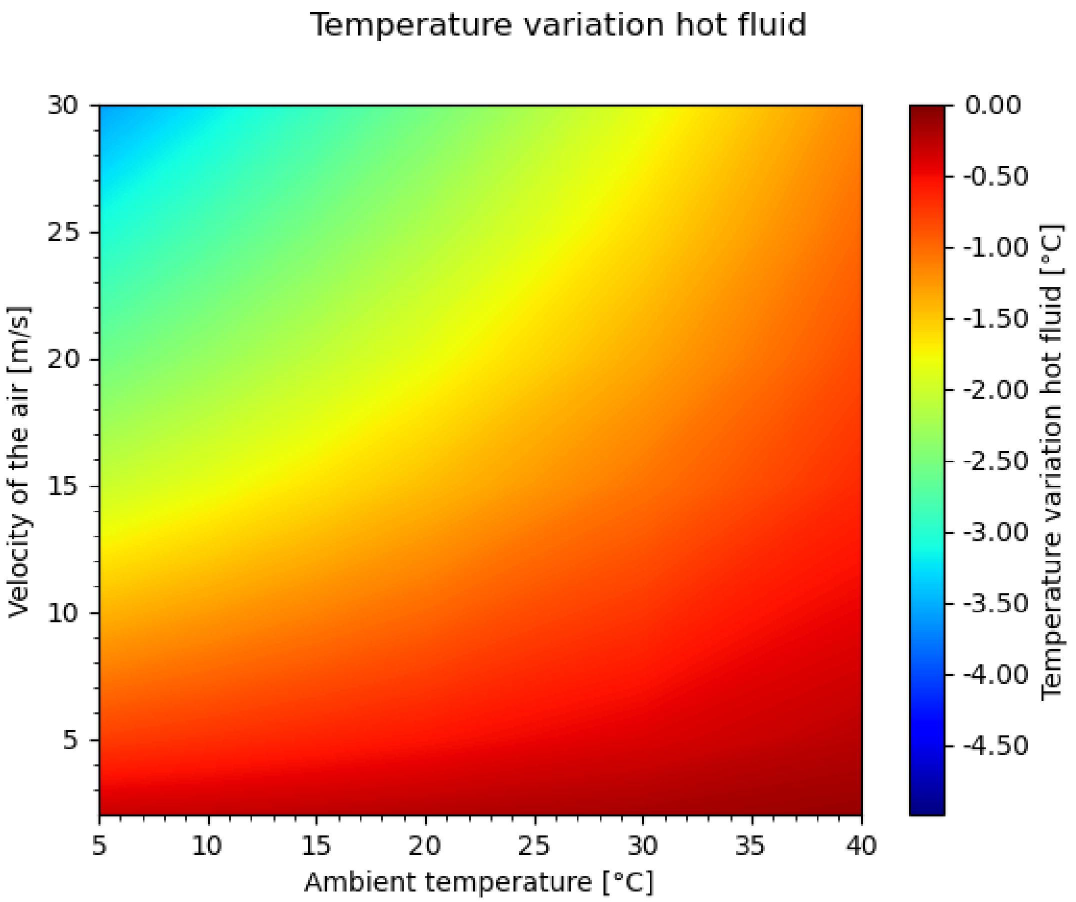


Figure 29: Temperature variation hot fluid at 2000 meters

10 Refill of the water tank

The refill of the water tank is one of the main operations that are needed during the functioning of the electrolyzer: the water is consumed during the hydrogen production, and it has to be replaced in the loop. Varying the frequency at which the refill is done and the temperature of the tap water, it changes the temperature of the electrolyte inside the tank. A different temperature after the refilling in the tank means a different water temperature that goes into the stack: this leads to a different voltage of the cell and so to a different power of the stack.

This part is very interesting to see which the best solution is to have the lowest power consumption for the stack.

10.1 Variance of the time of refilling

Knowing the volume of the tank, it is essential to know how much water is consumed during the reaction and this is possible thanks to the stoichiometry reaction:

$$\mathrm{H_2O} \rightarrow \mathrm{H_2} + \frac{1}{2}\,\mathrm{O_2}$$

From this reaction it is possible to see that the moles of water consumed are equal to the ones of hydrogen produced:

$$n_{H2O} = n_{H2} \qquad [\,78\,]$$

So using the molar weight o the water, the mass flow rate of the water consumed per hour can be calculated as:

$$Vol_{H2O} = (n_{H2O} * MM_{H2O} * 3.6) \quad [\,79\,]$$

- MM_{H2O} : molar weight of the water [g/mol]
- 3.6: coefficient to pass from [g/s] to [L/h]

To calculate this value, it is possible to use a Python code with the following data:

- Current density
- Number of cells: 23
- Voltage of the cell: 2.4[V]
- Active area of the cell: 50 [cm^2]

Using these data in the electrochemical model the following result is obtained:

$$Vol_{H2O} = 0.4\ [\frac{L}{h}]$$

The result obtained shows the quantity of water consumed in one hour to obtain a certain amount of hydrogen. The quantity of KOH inside the tank remains constant, it is not consumed from the reaction of hydrogen formation.

Once this value is known, the volume of water that has to be refilled is the following one, given by the formula:

$$DeltaV = Vol_{H2O} * n_{hour} \quad [80]$$

- n_{hour}: Number of hours after which the refill is done

From this equation, the quantity of water that has to be refilled is directly proportional to the hour at which the refill is done as the number of hours grow also the volume that has to be refilled becomes bigger.

Having fixed a volume of the tank, the volume of electrolyte that is in the tank when the refill has to be done is equal to:

$$Vol_{final} = Vol_{tank} - DeltaV \quad [81]$$

- Vol_{tank} : volume of the tank [L]
- Vol_{final} : volume of water in the tank when the refill has to be done [L]

This quantity of water Vol_{final} is considered at a temperature equal to the one of the electrolytes exiting the heat exchanger, so more or less at 55°C. The properties of the electrolyte are calculated using formulas above in the paragraph ‘Electrolyte’, considering a percentage of KOH in the water equal to 1%.

In this way the volume of the water that has to be refilled is calculated and varies with the time at which the refill happens. It is interesting now to also calculate the variance of the water temperature that is in the tank.

The formula to calculate the temperature of the fluid inside the tank after the refilling is the following one:

$$T_{refill} = \frac{mass_{el-tank} * Cp_{el\_tank} * T_{el\_tank} + mass_{H2O\_refill} * Cp_{H2O\_tank} * T_{H2O\_tank}}{mass_{el-tank} * Cp_{el_{tank}} + mass_{H2O\_refill} * Cp_{H2O\_tank}} \quad [82]$$

- $mass_{el-tank}$: mass of electrolyte inside the tank before the refilling [kg];
- $mass_{H2O\_refill}$: mass of tap water that is inserted during the refill [kg];
- Cp_{el_tank}: specific heat at constant pressure of the mass of electrolyte inside the tank before the refilling [J/kgK];

- Cp_{H2O_tank}: specific heat at constant pressure of the mass of tap water that is inserted during the refill [J/kgK];
- T_{el_tank}: temperature of the electrolyte inside the tank before the refilling [K];
- T_{H2O_tank}: temperature of the tap water that is inserted during the refill [K].

The temperature after the refilling is the temperature at which the electrolyte is sent into the stack and so is the operational fluid. If this latter decreases until a certain temperature (ex 45 °C), it has to be warm up to a certain level of temperature: the heat in advance from the stack is no more sufficient and so some additional heat has to be sent into the tank to heat this water. A good solution could be put an additional iter to warm up the water that has to be sent into the stack.

To see which is the variance of the temperature after the refilling, a fixed tap water temperature was fixed equal to 30 °C and the minutes of the refilling are changing. In the next graph is possible to see how the temperature of the water after the refill varies with the time at which the refill is done (Figure 22):

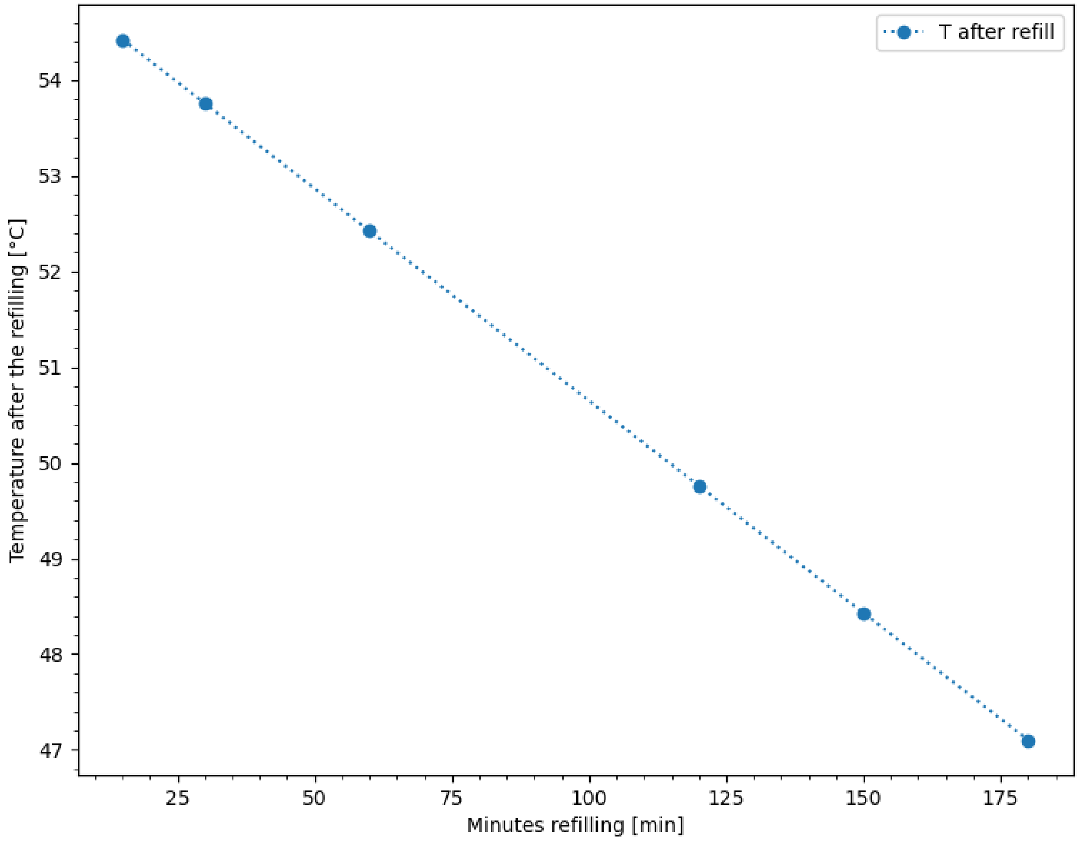


Figure 30: Electrolyte temperature after the refilling varying time of refilling

From the graph is possible to see that the temperature of the electrolyte after the refill decreases at the growth of the time after which the refill is done this is due to more water is inserted at 30°C and so the temperature inside the tank decreases more. If the temperature of the water inside the tank decreases too much,

For this reason, the refill should be done often and with smaller water quantities than after a long time with bigger water quantities.

10.2 Variance of tap water temperature and time for refilling

A very important study and more in deep than the previous one is the study about the variance of both tap water and time at which the refill must be done.

This study is very important, especially because this type of electrolyzer can be sold in different areas of the World and for this reason the water that is inserted during the refill can be at different temperature from region to region. So, for this part of the project were selected temperatures between the 10 °C and 55 °C, which is the highest water temperature for what concern the tap water.

The temperature, together with the current density, is the main parameter that influences the voltage of the cell, and so consequently the power of the stack. From the theory it is known that the voltage of the cell grows at the decrease of working temperature of the fluid.

The map of the changing ot the temperature of the electrolyte after the refilling is shown in Figure 23:

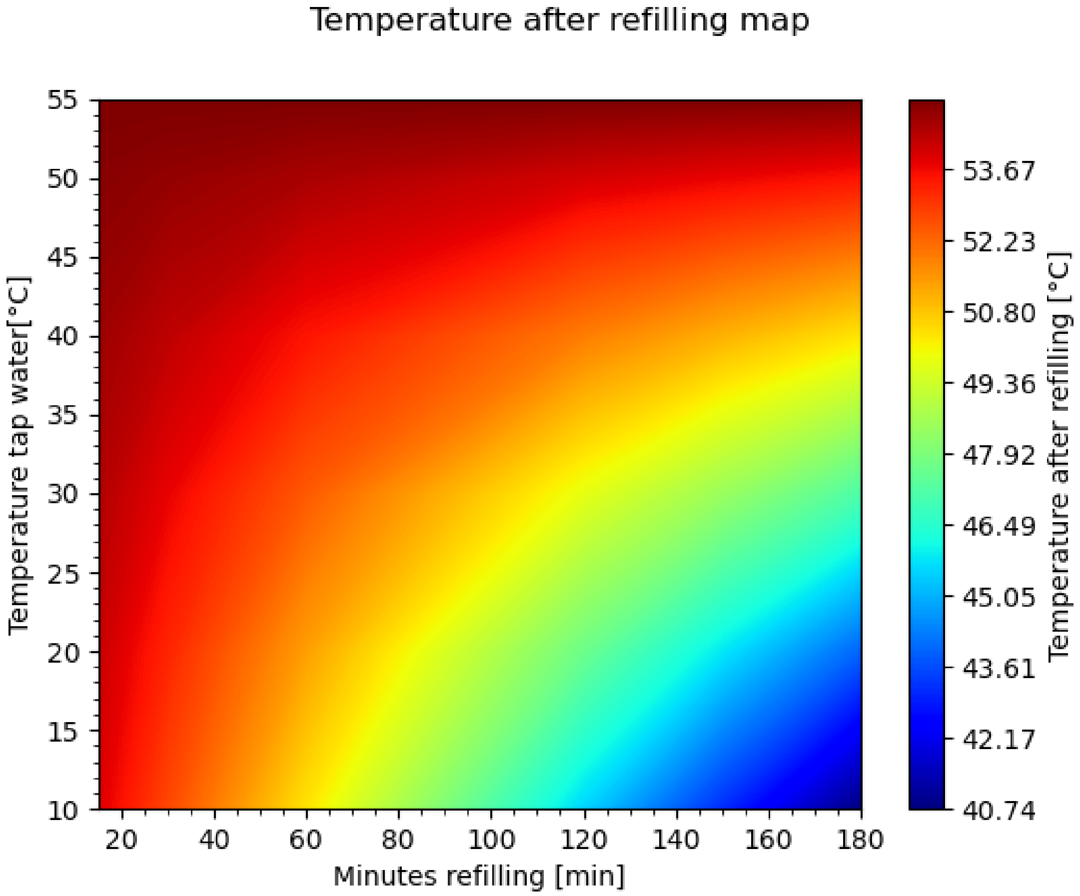


Figure 31: Electrolyte temperature after the refilling

So the voltage of the cell, depending on the temperature of the water that is sent into the water tank and on the time after which is done the refill, it grows in percentage with the following results (Figure 24):

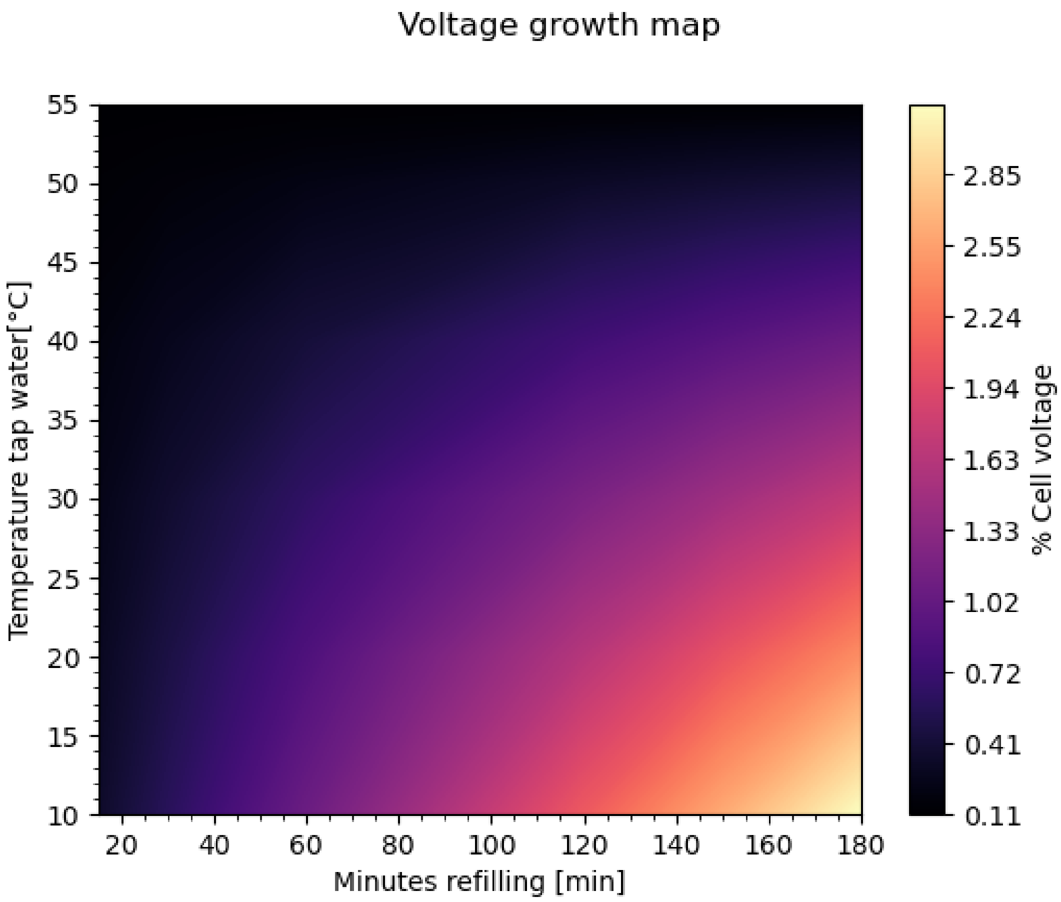


Figure 32: Voltage growth

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As it is possible to see, the voltage of the cell has the minimum value when the water temperature is the lowest one and when the time of refilling is the highest one: this means a temperature of the electrolyte in the tank after the refilling lower.

The power is directly proportional to the voltage, and so there’s a percentual increase in the power of the stack too (Figure 25):

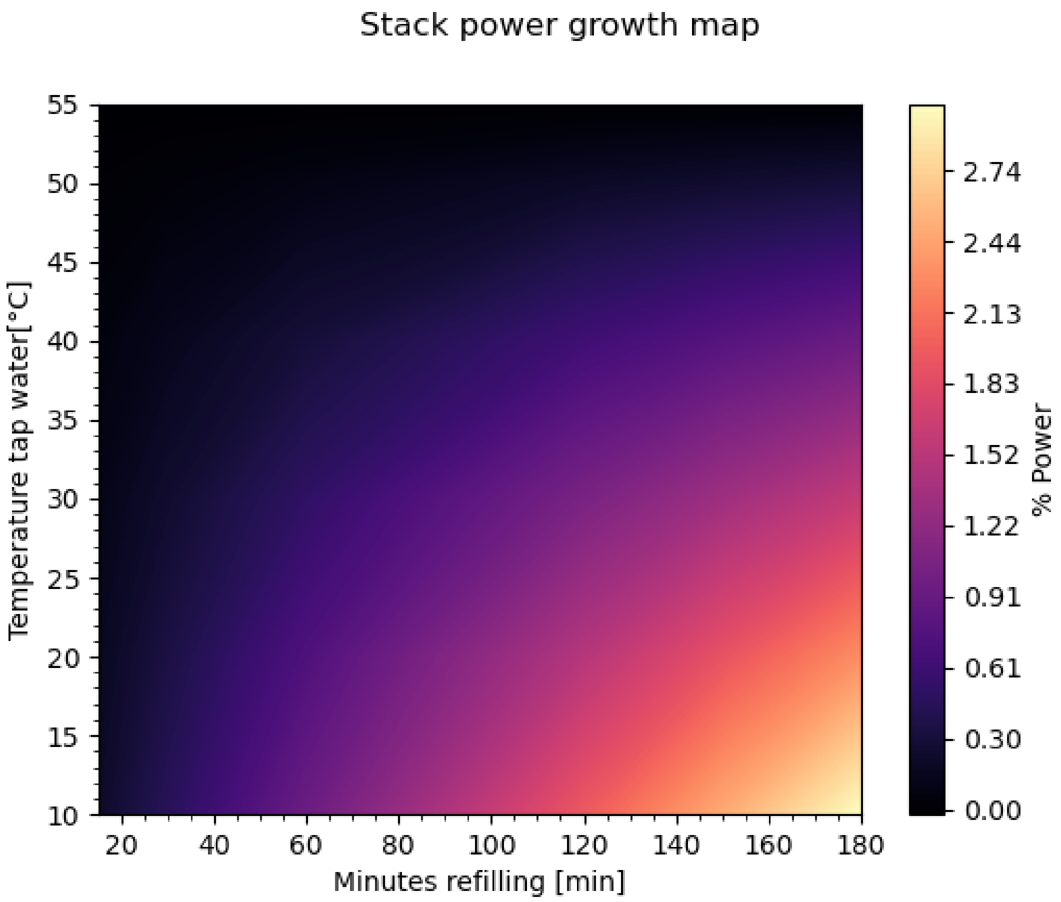

Figure 33: Stack power growth

A growth in the voltage and consequently in the power means that a bigger power is needed from the PSU, so more money has to be spent.

10.3 Results

This study shows that the refill of the tank must be done more often and with smaller quantities of water: this especially for what concern the voltage. This latter becomes higher with the operational temperature decrease and this leads to a bigger power that has to be sent to the stack from the PSU.

Another negative point is that if the water temperature in the tank decreases too much under a certain level, an iter should be used to heat it, and so it would be needed more power from the PSU to activate it.

11 Try to find an optimum between the developments of this thesis

Once all the results of the study have been obtained, an optimisation can be carried out. Why is optimisation used? For example, to identify a system design for maximum performance, or to determine operational parameters that maximise system performance. It also identifies best and worst-case scenarios (such as the greatest damage that can be caused) and identifies the minimum costs of the system design and operating parameters.

The following are some optimisation cases that can be implemented on this thesis study.

11.1 Possible optimizations

In this pre-design model, the means have been given to calculate the dimensions of the various components as certain parameters vary and to optimise certain design choices, such as the time after which refilling must be carried out so that the temperature inside the water tank remains as high as possible. The time, as seen above, is better to be as small as possible so as not to have a large temperature delta inside the tank.

The same could be done when considering the heat exchanger: its size is directly proportional to the power of the stack, since it defines the amount of electrolyte that must be cooled after passing through the stack. Here again, a major effect on the functionality of the HE is given by the environment in which it is located: in addition to the size of the heat exchange area, the fluid it cools is in fact air, and therefore depending on where the electrolyser is working, there will be a greater or lesser heat exchange between the fluids.

Except for these components, the former depending solely on the power of the stack and the latter also on the environment in which the electrolyser works, the same cannot be said for other components. With this pre-design of the electrolyser, in fact, it is possible to make an optimisation with respect to the parameter that matters most.

A possible optimisation could be done with respect to the waste area of the raw material: this latter is purchased in sheets, which are then cut in the laboratory slightly larger than the raw material needed. Not all of the sheet area is used, and some is lost. A possible optimisation could therefore concern the cost of the raw material waste: if one wants to save more on this component, one could see which size of raw material makes the cost of the descarded raw material as low as possible.

Analysing the areas considered during this thesis study, it can be seen from figure 17 that the lowest rejection cost occurs when the active raw material area is 50 cm^2, which is the smallest size used. This has a rejection cost of 22% of the total sheet cost. Therefore, by taking this measure of active area, for each power value one can obtain the number of cells needed for that given power. The number of cells will then influence the length of the stack, which will be the higher as the cells have a smaller area and therefore a greater number are required, and the weight of the stack. The latter is also higher than having a smaller number of cells with a larger active area, and the weight percentage of the component that matters most is that of the cells.

As far as the amount of electrolyte in the stack is concerned, it does not depend on the number of cells but, as mentioned before, only on the power of the stack: this means that the water tank doesn’t depend on the cell size.

This is one of the types of optimisations that can be done using this pre-design template, but other optimisations could be made. There may be constraints about stack size and thus an optimisation could be performed by imposing the maximum stack length that can be had in that given situation. The same thing can be done for weight.

12 Conclusions

Summarizing, the aim of the study is to do a pre-design model of an AEM electrolyzer, analysing its dimensioning and optimizing some part of it.

Different models’ scripts have been used and were built in Python, where all the calculations were done. The models first were carried out with Enapter's electrolyzer data to test that they were valid, and only then were they analysed under different conditions and by changing some operating parameters. Thus, the results obtained from the theoretical models can be compared to the real ones from the company.

There was a great deal of research into documents and information, especially regarding the first models used: that relating to voltage and that relating to the properties of the electrolyte. In addition, a literature search was carried out for the calculation of the amount of electrolyte required at the stack inlet, analysing the EU harmonised protocols for testing of low temperature water electrolysers.

The impact of the weight of each individual component of the stack on the weight of the stack at a stack power of 3000W was studied, so it was possible to see how varying the active area of the cells also varies the impact on the weight of each individual component

As for the optimisation part, i.e., that of the cost of the raw material discarded area and that of the minutes after which to refill the water in the tank, these were carried out under the company's operating conditions and parameters.

On the other hand, input parameters were changed for the dimensioning, so that it was possible to analyse how the output and size of the electrolyser varied, changing so the pipes, the water tank and heat exchanger sizes.

The optimisations that can be made through this thesis study are manifold, concerning economic or structural parameters. It can be adopted on any stack power and environmental conditions, making it useful to see how the electrolyser can work in different areas of the world with different climatic conditions.

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