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ANALYSIS OF SEAWATER ELECTROLYSIS TECHNOLOGIES FOR GREEN HYDROGEN PRODUCTION

Dissertation Report of the Master's Degree in Biological and Chemical Engineering

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JURY

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Resumo

O objetivo deste estudo é compreender a viabilidade técnica e económica da instalação e operação de uma central de desalinização para fornecer água a um processo de eletrólise de água de larga escala (GW). A central de produção de hidrogénio deve ser alimentada por fontes renováveis tais como energia eólica e solar fotovoltáico. A divulgação de investimentos significativos na produção de hidrogénio na região de Sines torna importante a análise detalhada da operação deste tipo de sistema que acarreta desafios relativamente às reservas de eletricidade e água. Água, em particular água doce, é um recurso escasso na zona sul de Portugal e a instalação de uma indústria que usa grandes quantidades de água nos processos pode causar pressão considerável nas reservas existentes.

Dada a proximidade da região ao Oceano Atlântico, é relevante avaliar a instalação da central de desalinização e analizar o impacto geral dessa opção na produção de hidrogénio.

A operação da unidade de desalinização é analizada do ponto de vista técnico, ao considerar que é necessário produzir água para fornecer as necessidades instantâneas do eletrolizador. Isto é feito ao dividir um ano em intervalos de uma hora e estimar a quantidade de água a produzir em cada hora, considerando a eficiência da dissociação de água do eletrolizador. A unidade de desalinização é ajustada para utilizar o máximo dos excessos de produção de eletricidade das fontes de energia renováveis que alimentam o eletrolizador.

Do ponto de vista económico, dois parâmetros foram analizados. Primeiro o custo nívelado de água desalinizada é estimado e comparado com o custo de água da rede. Verificou-se que o custo nívelado de água desalinizada é inferior ao custo de água potável fornecida às indústrias locais pelo serviço municipal de águas de Sines (Águas de Santo André).

Segundo, o impacto no custo nivelado de hidrogénio é analizado. Verificou-se que a instalação e operação da unidade de desalinização aumenta o custo nivelado de hidrogénio por menos de 1%.

Desalinização de água do mar demonstra ser uma alternativa tecnicamente e economicamente viável para produzir água para uma central de eletrólise de larga escala que poderá aliviar a pressão de fontes locais de água doce.

Abstract

The goal of this study is to understand the technical and economic feasibility of installing and operating a seawater desalination plant to supply water to a GW-scale water electrolysis process. That hydrogen production facility should be powered by dedicated renewable energy sources such as wind and solar photovoltaic. The announcement of significant investments in hydrogen production in the Sines region makes it relevant to perform a detailed analysis of the operation of this type of system that will present challenges with regards to the electricity and water supply. Water, in particular freshwater, is a scarce resource in the south of Portugal and the installation of an industry that uses large amounts of water as feedstock can place considerable pressure on existing reserves.

Given the proximity of the region to the Atlantic Ocean, it is appropriate to evaluate the installation of a desalination plant and analyze the overall impact of that option on hydrogen production.

The operation of the desalination unit is analyzed from a technical point of view, by considering that water must be produced to provide the instantaneous needs of the electrolyzer. This is done by dividing one year in one-hour slots and estimating how much water must be produced each hour, considering the water dissociation efficiency of the electrolyzer. The desalination unit is adjusted to make the best use of the excess electricity production of the renewable energy sources that feed the electrolyzer.

From the economic point of view, two parameters are analyzed. First the levelized cost of desalinated water is estimated and compared to the cost of grid water. It has been found that the levelized cost of desalinated water is lower than the price of potable water supplied to the local industries by the Sines municipal water service (Águas de Santo André).

Second, the impact on the levelized cost of hydrogen is analyzed. It is shown that the installation and operation of the desalination unit increases the levelized cost of hydrogen by less than 1%.

Seawater desalination is shown to be a technically and economically viable alternative for producing the water feedstock for a GW-scale electrolysis facility that could alleviate pressure on local freshwater sources.

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Symbols and abbreviations

CAPEX – Capital expenditure

CER – Chlorine Evolution Reaction

CH_4 – Methane

CO – Carbon monoxide

CO_2 – Carbon dioxide

DGEG – Directorate-General for Energy and Geology

EU – European Union

FOWS – Forward-osmosis Water Splitting

GHG – Greenhouse gas

H_2 – Molecular hydrogen

KOH – Potassium hydroxide

Kt – Kilotons

LCOH – Levelized Cost Of Hydrogen

LCOW – Levelized Cost Of Water

MSFD – Multi-stage Flash Distillation

NaOH – Sodium hydroxide

OER – Oxygen Evolution Reaction

OPEX – Operational expenditure

PEM – Polymer Electrolyte Membrane

PNEC 2030 – Plano Nacional Energia Clima 2021-2030

PV – Photovoltaic

R & D – Research and Development

RES – Renewable Energy Source

RO – Reverse Osmosis

1. Introduction

With the rising concerns about climate change there has been much effort in the investigation and development of sustainable energy production, to reduce the damage caused by energy generated from non-renewable sources. Ideally these new sustainable technologies reduce greenhouse gas (GHG) emissions caused by burning fossil fuels, which contribute to the increase of global temperature, and other pollutants that damage the environment, such as fine particles and carbon monoxide. The Paris Agreement has concluded that until year 2100 the effort should be put into reducing greenhouse gas emissions, to contain the global temperature increase within 1.5ºC above pre-industrial levels[1].

The European Commission stance towards the reduction of GHG emissions has been very strong over the last years. A new strategy that aims to cut down emissions, the European Green Deal[2], has been proposed for the European Union countries, through the use of innovative, environmentally friendly technologies that will work on decarbonizing the energy sector.

The main goals of the European Green Deal are the following:

1. A climate neutral Europe - the EU aims to reach net-zero GHG emissions by 2050, through a series of laws and regulations in the energy sectors;
2. Circular economy - using cleaner resources and reusing materials, which includes changes in carbon-intensive industries, such as cement or steel producing industries;
3. Building renovation - improvements in housing that lessen the use of energy, such as reducing the need for heating, which is responsible for 40% of the energy consumption in the EU;
4. Zero pollution - the EU intends to minimize all forms of pollution, whether air, ground or water, through measures such as new waste management laws;
5. Ecosystems & biodiversity - fight deforestation and any other forms of ecosystem loss, by fighting water and soil pollution and adopting new forest strategies both in the cities and countryside;
6. Farm to fork strategy - the EU also intends to improve agriculture through the use of less fertilizers, pesticides and antibiotics, promoting a "greener" type of agriculture;
7. Transport - new CO_2 emission standards are proposed to tackle GHG emissions, by using electric cars and alternative and sustainable fuels in other types of transportation, including aviation and heavy duty transportation;
8. R & D and innovation - the EU will fund climate friendly technologies that are being researched and developed to be alternatives, or innovations, to the current energy system;
9. External relations - The EU will mobilize its diplomatic efforts with other non EU countries in support of the Green Deal, through measures such as the implementation of a carbon border tax;

In order to implement these proposals the European Union will provide funding and technical support to the EU member states. The program of the Just Transition Mechanism

(JTM) was proposed on 28th May 2020, where €150 billion will be mobilized in order to assist European countries transitioning to better alternatives, in particular regions, workers and industries that face greater challenges with the transition (regions that are carbon-intensive and workers of fossil industries). As such many measures will be taken, for instance new opportunities will be given to workers, and more attractive conditions will be created to attract investors in these sectors[2].

In the framework of the European Green Deal, the European Commission proposed the adoption of strategic plans by all EU member states, most important of which being the National Energy and Climate Plan 2021-2030 (Plano Nacional de Energia e Clima 2021-2030, PNEC 2030), the Clean and Sustainable Mobility Plan, and Clean Energy Plan.

Portugal committed to the goal of achieving carbon neutrality by year 2050, on 30th September 2016, after ratifying the Paris Agreement. In the following years the 2050 Carbon Neutrality Roadmap (Roteiro para a Neutralidade Carbonica 2050, RNC 2050) started being developed, and presented at the end of 2018. Later, in January 2019, Portugal's PNEC 2030[3] was presented, to ensure that the proposals related to energy and climate are fulfilled until 2030.

The main goals proposed by the PNEC 2030[3] are the following:

- Reduction of GHG emissions - The PNEC 2030 proposes a general reduction of GHG emissions of -45% to -55% in relation to 2005;
- Energy efficiency - The energy efficiency should be improved in order to decrease energy use and GHG emissions, reducing the primary energy consumption by 35%;
- Increase the use of renewable energies to 47% of gross final energy consumption;
- 20% renewable energy in transport;
- Increase in electrical interconnections to 15%, promoting a greater flow between electrical grids in Europe;

Specifically, eight national goals were set in order to better fulfill the objectives of the PNEC 2030. These goals are strongly related to the main proposals of the PNEC 2030 and are the following:

1. Decarbonization of the national economy - The PNEC proposes a reduction of GHG emissions in all sectors, namely energy and industry, mobility and transport, agriculture and forests, and general waste and wastewaters, and promoting the integration of mitigation objectives in the sectoral policies;
2. Prioritize energy efficiency - The primary energy consumption of all sectors should be reduced to promote sustainability, as well as an efficient use of resources. Energy efficiency should be sought by the rehabilitation and renovation of buildings and the promotion of zero emission buildings;
3. Reinforce the use of renewables and reduce energy dependence - The diversification of energy sources using renewables should be reinforced, promoting a greater electrification of the economy;
4. Guarantee the security of supply - The reinforcement, modernization and optimization of energy infrastructures should be guaranteed, ensuring the maintenance of a flexible energy system;

5. Promote sustainable mobility – Decarbonization of the transport sector by promoting modal shifts, electrical mobility (both private and collective transport) and the promotion of alternative renewable fuels;
6. Promote sustainable agriculture and foresting and increase carbon sequestration - The carbon footprint of agricultural practices should be reduced, and the agricultural and forest sectors should be improved to increase carbon sequestration;
7. Development of an innovative and competitive industry - The industry sector should be modernized by supporting innovation, decarbonization, digitalization, and circularity, promoting economic competitiveness;
8. Ensure a just, democratic and cohesive transition - The responsibility of each citizen as an active contributor in the energy transition and decarbonization should be reinforced, equal conditions should be given to all, energy poverty should be fought, and vulnerable citizen protection should be assured;

In the EU there has been an increase in the use of renewable energies for energy production since 2005. In the EU, Portugal greatly uses renewable energies, making up a total use of 34.0% by 2020. This makes Portugal the 5th country in the European Union that uses most of its energy from renewable technologies, standing behind Sweden (60.1%), Finland (43.8%), Latvia (42.1%) and Austria (36.5%), in 2020[4].

There are several reasons for Portugal to invest in renewable energies, aside from increasing sustainability and reducing pollution. The geography and general climate of Portugal allow for an efficient harvest of energy, in particular solar, wind and hydric power. And this increased renewable electricity production capacity can be used for producing renewable fuels such as hydrogen.

The current National Hydrogen Strategy (Estratégia Nacional para o Hydrogénio, EN-H2)[5] intends to promote a gradual use of hydrogen in the Portuguese energy and economic systems by introducing the necessary requirements for the regulations, security, technology and financing of the projects. The key initiatives of this strategy are the creation of a main project for green hydrogen production in Sines, the decarbonisation of the heavy transport sector, the decarbonisation of the national industry, the creation of a collaborative hydrogen laboratory, and the application to IPCEI (Important Projects of Common European Interest) Hydrogen.

The strategy also encourages the investment of industries in hydrogen by ensuring that there are short to long term outcomes for its production or use, both for ongoing and starting projects. By ensuring there is a solid framework and outcome, there should be an increase in public, national and international support for projects related to the use of hydrogen.

This strategy was designed to improve the transition to renewable energies in specific sectors that would otherwise be too much of a challenge in economic or technical terms, such as industries that make intensive use of heat in their processes. The strategy should assist Portugal in its fulfillment of the PNEC 2030 since it proposes approaches to reduce carbon emissions, by promoting the most economic ways to introduce hydrogen in the Portuguese energy market.

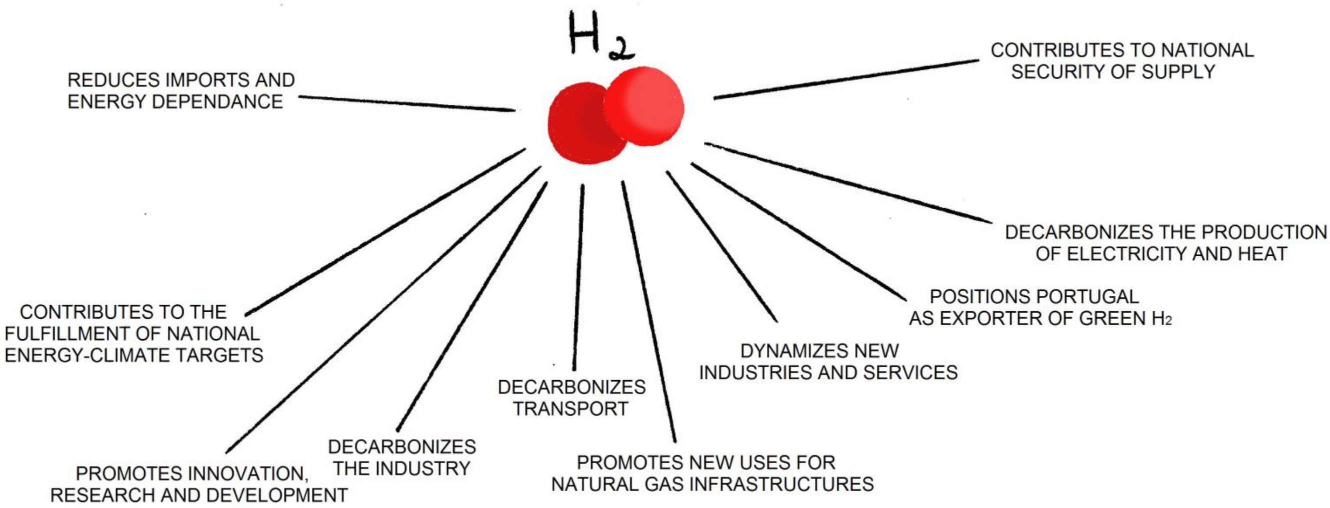

Figure 1 - Several advantages of the use of Hydrogen as a vector for decarbonization (author)

The use of hydrogen (schematized in figure 1) brings many advantages since it's an alternative to fossil fuels that can be produced using renewable sources of energy (green hydrogen production) therefore, reducing the greenhouse gas emissions. Some of the advantages of using hydrogen are the fact that it's a stable molecule that allows the storage of renewable energies for a long time (bypassing the problems of intermittence from certain renewable energy sources), it decreases the need for importing energy from other countries, it reduces the greenhouse gas emissions from other economic sectors (such as refining industries, cement industries, ceramic industries) by replacing the use of fossil fuels, promotes small scale energy production (in remote or isolated areas, or in off-grid applications) and promotes economic and job growth due to the development and maintenance of the technologies associated with its production[3,5].

In order to achieve such goals, a green hydrogen production industry must be established. The most ambitious project to date is the Sines Industrial Project. In Sines, a city in south of Portugal (coastal Alentejo), there was a thermoelectric coal plant that ended operation in the beginning of 2021. In response to that a hydrogen production plant based on water electrolysis will be built, with a total capacity of 1GW, sustained by Renewable energy sources (RES). This project is set to be completed by 2030[5].

The water electrolysis process requires freshwater. While sea water can be used for the water electrolysis it is known to quickly corrode the equipment, due to its dissolved salts. Therefore in order to avoid water electrolysis using freshwater (a valuable resource) or sea water (which damages the equipment), a desalination process can be used to obtain fresh water for the water electrolysis. This is a viable option considering the proximity of Sines to the sea and the relative simplicity of introducing a desalination unit to an electrolysis unit. The proposed desalination unit should run on RES, much like the electrolyzers.

This dissertation intends to study the viability of such proposal. The work is divided on five chapters, starting with the introduction to present the goals of this project and other related projects. The second chapter is the state of the art where a bibliographical study is presented to highlight the current situation of the technologies related to this project, such as the water electrolysis and desalination technologies. The third chapter describes the energy modeling software used for the dissertation and the methods for obtaining the technical and economical results. The fourth chapter describes and analyses the technical results and economical results. The final chapter brings the conclusions of the work and possible further work.

2. State of the art

2.1. Hydrogen

To respond to the growing energy needs and to reduce the use of non-renewable energies alternative sources have been proposed, namely hydrogen (in its molecular form, H_2). Hydrogen has many potential uses: it can be used to power vehicles, it can be used as an energy carrier and for storage (to fill the gaps of intermittent power sources such as solar power during the night), or feedstock in certain industrial processes such as green methanol production. Green hydrogen production (hydrogen produced from renewable energies) is growing, as technologies are scaling up[6]. Due to its several uses, hydrogen is regarded as a key substance to replace fossil fuel energy[7].

Atomic hydrogen is the simplest chemical element, having the atomic number 1 and the atomic weight of 1.008 g/mol, it is the lightest element in the periodic table. It's also commonly found in most chemical substances, being the most common element of the entire universe[8]. However, significant quantities of molecular hydrogen (H_2) can only be obtained using industrial processes. The reason for this is because hydrogen, especially in its monatomic allotrope, tends to form bonds with other atoms and molecules. This makes it necessary to separate the hydrogen atoms from certain compounds, such as water. The main characteristics of molecular hydrogen are found in Table 1.

Table 1: Main characteristics of molecular Hydrogen[8]

	Value	Unit
Molecular weight	2.016	g/mol
Melting point	-259.16	◦C
Boiling point	-252.879	◦C
Density (STP)	0.089	kg/m^3
Density (at melting point/boiling point)	0.07	kg/m^3
Specific Energy (higher heating value)	141.86	MJ/kg
Specific Energy (lower heating value)	119.93	MJ/kg
Oxidation states	-1,+1	

2.2. Methods of Hydrogen Production

There are several methods of hydrogen production, as listed below.

2.2.1. Steam Methane Reforming

There are many methods to obtain hydrogen from separations, the most common being Steam Methane Reforming (SMR), an endothermic process where methane is heated with water vapor, producing large amounts of hydrogen. While methane is the most widely used feedstock for this process, other compounds can be used to obtain hydrogen, such as ethanol and propane. Since the process requires heat, energy must be supplied. While it is an economically viable method, it produces greenhouse gases such as CO_2 and CO. The equilibrium reaction equation is the following[9]:

$$CH_4 + H_2O \ + heat \ \leftrightarrow CO + 3H_2 \qquad (1)$$

The reaction is followed by a process called “water gas shift reaction” where the carbon monoxide and steam react to form carbon dioxide and more hydrogen. The equation for the water gas shift reaction is the following:

$$CO \ + \ H_2O \ \rightarrow \ CO_2 \ + \ H_2 \qquad (2)$$

2.2.2. Partial Oxidation

Partial Oxidation is another chemical method of obtaining hydrogen through fossil fuels. This technology consists of achieving a partial oxidation of a fossil fuel with oxygen through its combustion, producing both hydrogen and carbon monoxide. A fossil fuel such as methane is used. As such, it is a method which causes carbon emissions. The reaction equation for the methane oxidation is the following:

$$2CH_4 + \ O_2 \ \rightarrow 4H_2 + \ 2CO \qquad (3)$$

2.2.3. Methane Pyrolysis

Another chemical method for obtaining hydrogen is the Methane Pyrolysis, which like the SRM uses methane as a feedstock. It does not emit CO_2 or other greenhouse gas, however, since the reaction only produces solid carbon and hydrogen. The reaction equation is the following:

$$CH_4 \rightarrow \ 2H_2 \ + \ C \qquad (4)$$

2.2.4. Fermentative Hydrogen Production

There are biological methods which cause little or no pollution, such as the Fermentative Hydrogen Production that rely on biochemical processes such as fermentation. However, these processes yield little hydrogen compared to the other industrial processes, therefore cannot be used in large scale hydrogen production. The reaction equation for dark fermentation of glucose (fermentation in the absence of light) which is converted to acetic acid, is the following:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3CO_2H + 2CO_2 + 4H_2 \qquad (5)$$

2.2.5. Electrolytic Processes

Among the electrochemical methods, the most commonly used is the electrolysis of water (figure 2). Electrolysis is a redox reaction, where a process of transfer of electrons dissociates the water molecule producing both hydrogen (H_2) and oxygen (O_2) molecules. This method has many advantages considering its efficiency and relative affordability. Unlike many other industrial processes, the electrolysis process works at normal pressure. Two very efficient electrolysis technologies are the Alkaline Water Electrolysis (AE) and the Polymer Electrolyte Membrane (PEM) Electrolysis.

The main components of an electrolysis cell (AE or PEM) are:

- Electrolyte - The electrolyte is an ionic substance necessary to supply positive and negative ions (cations and anions respectively) to the reaction. Depending on the technology used, the electrolyte can either be a liquid (such as potassium hydroxide) or solid (such as perfluorosulfonic acid). The ions are attracted by the electrodes;
- Electrodes - Two electrodes, the cathode and anode, attract the ions. The produced hydrogen leaves through the cathode side of the cell. An electrocatalyst can be present to improve the efficiency of the electrodes;
- Physical barrier - The physical barrier can either be a diaphragm or a polymer membrane, and it is used to keep the hydrogen and oxygen separated. The barrier should be permeable to ions;

The global reaction of electrolysis is the following:

$$H_2O \rightarrow \frac{1}{2}O_2 + H_2 \qquad (6)$$

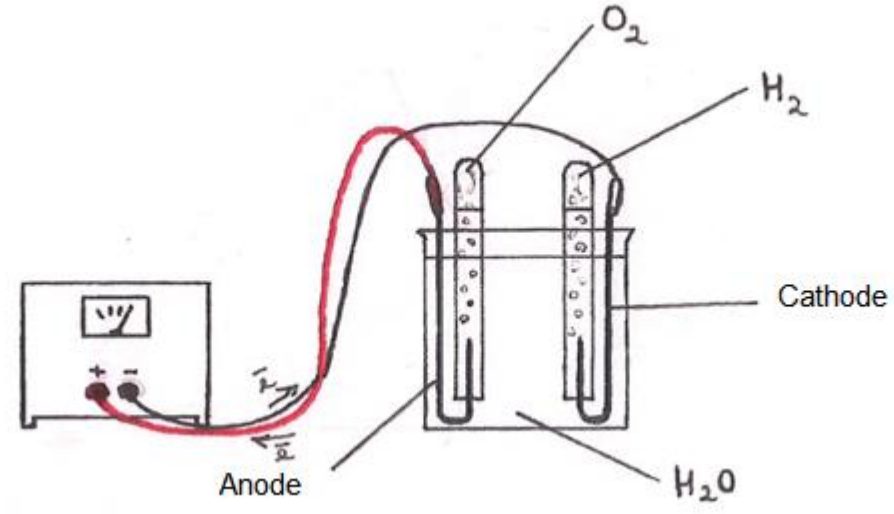

Figure 2 - Simple electrolysis process (author)

Each electrolysis technology has its chemical reaction, so the equation for each reaction is different.

The reaction responsible for the formation of hydrogen is called Hydrogen Evolution Reaction (HER), while the reaction where oxygen is formed is called Oxygen Evolution Reaction (OER). Electrocatalysts are usually present to improve the reactions, for instance platinum catalysts are usually present in HER. Besides platinum, electrocatalysts can be made of other materials, metal or non-metal, such as phosphides[10], transition metal nitrides[11] and carbides[12,13], among others. Electrocatalysts work by modifying the surface orbital nature, allowing for a higher electron count and thus improving the reaction.

In AE, the reactions are:

Cathode reaction (HER): $2H_2O(l) + 4e^- \rightarrow 4OH^-(g) + 2H_2(g)$ (7)

Anode reaction (OER): $4OH^-(g) \rightarrow 2H_2O(l) + 4e^- + O_2(g)$ (8)

In PEM, the reactions are:

Cathode reaction (HER): $4\,H^+\,(aq) + 4\,e^- \rightarrow 2H_2(g)$ (9)

Anode reaction (OER): $2\,H_2O(l) \rightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-$ (10)

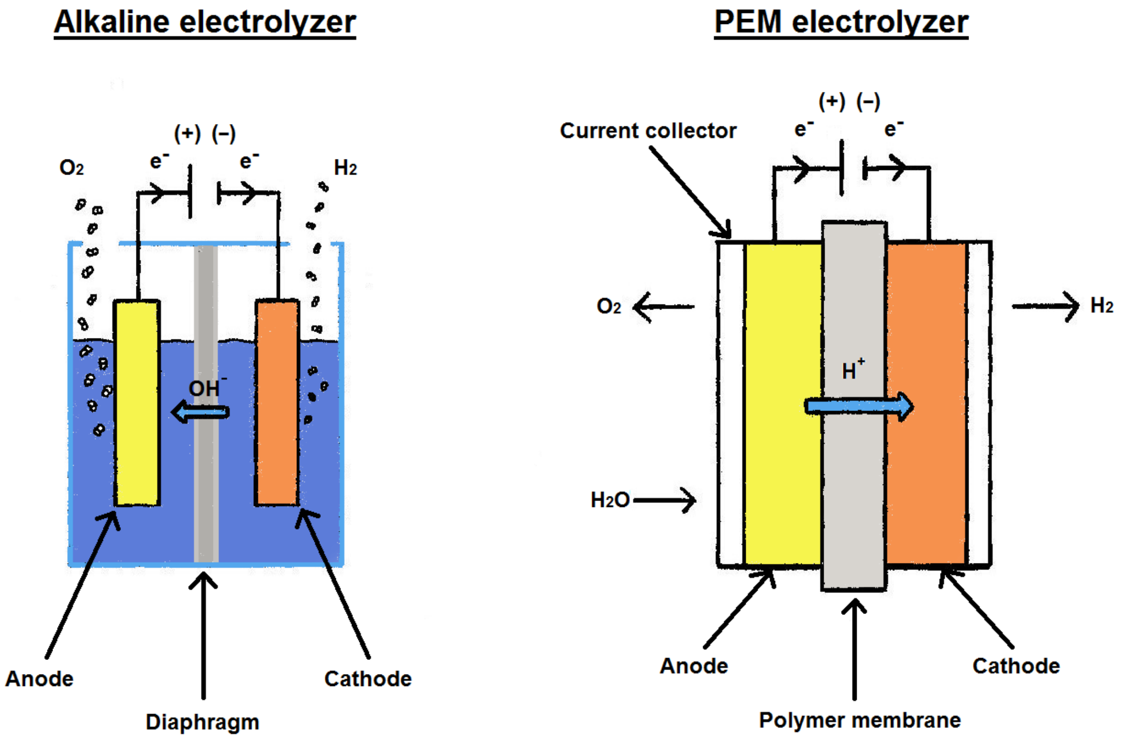

Figure 3 - Alkaline Electrolyzer and PEM Electrolyzer (author)

During the electrolysis process it is necessary to have a physical barrier, such as a diaphragm, to keep the gases properly separated. If there is no barrier the H_2 that is produced can migrate from the cathode and mix with the O_2, forming a mixture of H_2 and O_2, which is undesirable. A diaphragm is necessary for an alkaline electrolyzer to avoid mixtures. If a solid electrolyte is used a barrier is not necessary since the electrolyte itself can work as a reactant barrier to the H_2 and O_2. This is the case for the PEM electrolyzers, where the polymer membrane works as a barrier (figure 3).

The reaction of electrolysis, which consists of splitting a water molecule into molecular hydrogen and oxygen, requires energy, more specifically electric energy and thermal energy. If the thermal energy is increased, less electrical energy is necessary for the reaction[14], and vice-versa.

The potential difference between the two electrodes must be at least 1.23 V to electrolyze the water, in normal temperature and pressure conditions[15].

In order to split 1 mole of water molecules into 0.5 moles of molecular oxygen and 1 mole of molecular hydrogen the energy that is required can be defined by standard molar enthalpy, ΔH. The equation for this relation is the following:

$$\Delta H = \Delta G - T\Delta S \qquad (11)$$

, where ΔG is the molar Gibbs energy of water decomposition and ΔS is the molar entropy of water splitting reaction.

The molar Gibbs energy value and the molar entropy value represent the minimum electric energy and heat necessary to split the water molecule, respectively. The electric energy is supplied by an electric generator, from which the electricity is obtained from an energy source (in the case of green hydrogen it is obtained from a renewable energy source), while the heat energy is supplied by the temperature of the reaction. Using the equation (11), the two electrolysis voltages can be calculated. The first value is the thermodynamic voltage (U_{rev}), known as the reversible voltage (the minimum necessary voltage for the reaction) and the second is the enthalpic voltage (U_{therm}), represented by equation (12) and (13):

$$U_{rev} = \frac{\Delta G}{nF} \quad (12)$$

$$U_{therm} = \frac{\Delta H}{nF} \quad (13)$$

, where

F - Faraday constant (F = 96.485 C mol^{-1});

n - Number of electrons that are exchanged (n = 2);

Water electrolysis reactions generally occur at standard temperature and pressure conditions (T = 25ºC and p = 1 atm). So at standard conditions the values of ΔG and ΔH are 237.22 kJ mol^{-1} and 285.8 kJ mol^{-1}, respectively. Therefore, the values of U_{rev} and U_{therm} can be calculated:

$$U_{rev} \sim 1.23\,V \quad (14)$$

$$U_{therm} \sim 1.48\,V \quad (15)$$

This means that the actual applied voltage, which is the enthalpic voltage is higher than the thermodynamic voltage required for water splitting by 0.25 V. It corresponds to the minimum overvoltage with respect to the reversible voltage to be applied to the electrolysis cell in order to start the water decomposition reaction.

The thermodynamic values of $\Delta_r G$, $\Delta_r H$, U_{rev} and U_{therm} vary according to the temperature. For example, the total energy demand (ΔH_1) sharply decreases once the temperature of 100ºC is reached, and then slowly increases as the temperature rises. The energy demand of these thermodynamic values either increase or decrease at 100ºC because of the changes of state of water. The same applies to the voltages once the temperature of 100ºC is reached.

The passing of the electrical current through the electrolysis cell produces an internal resistance which generates heat, in a process called Joule Heating. This heat that is generated promotes the electrolysis reaction, since it decreases the energy demand of the U_{rev}. The possible variations of voltage values lead to the following configurations of the cell voltage (U_{cell}):

- $U_{cell} < U_{rev}$ – there is no reaction;
- $U_{rev} < U_{cell} < U_{therm}$ – the reaction requires extra heat;
- $U_{therm} < U_{cell}$ – the reaction occurs and is exothermic;

2.2.5.1. Alkaline Water Electrolysis

The Alkaline Water Electrolysis, represented in figure 5, is an electrolysis technology where the electrolyte is an alkaline solution of either Potassium Hydroxide (KOH) or Sodium Hydroxide (NaOH) in water at a concentration range of 25-30%[16]. The addition of these salts allows a better transport of ions between the electrodes without their consumption.

This method is quite mature. There are industrial electrolyzers capable of yielding a maximum of 650 m^3H_2/h with a long equipment lifetime (which can work for tens of thousands of hours) and in continuous operation. As such, even though it's still being improved, this technology has an efficiency of about 70%.

While the parameters can be different, usually the electrolyzer works at atmospheric pressure and relatively high temperatures. For instance, some operate at a pressure of 1 atm and temperature of 80ºC, yielding a minimum and maximum amount of hydrogen in the range 50-485 m^3/h [17], depending on the parameters set (electrolyte solution 25% KOH, energy consumption ranges 4.1-4.3 kWh/H_2 Nm^3). The hydrogen purity can reach up to 99.9%.

In terms of current density, alkaline electrolyzer cells work poorly at very low current densities. The current density should be in the order of 0.3 A/cm^2 for higher efficiency. Commercial alkaline electrolysers can run with a current density of up to 0.4 A/cm^2 [18].

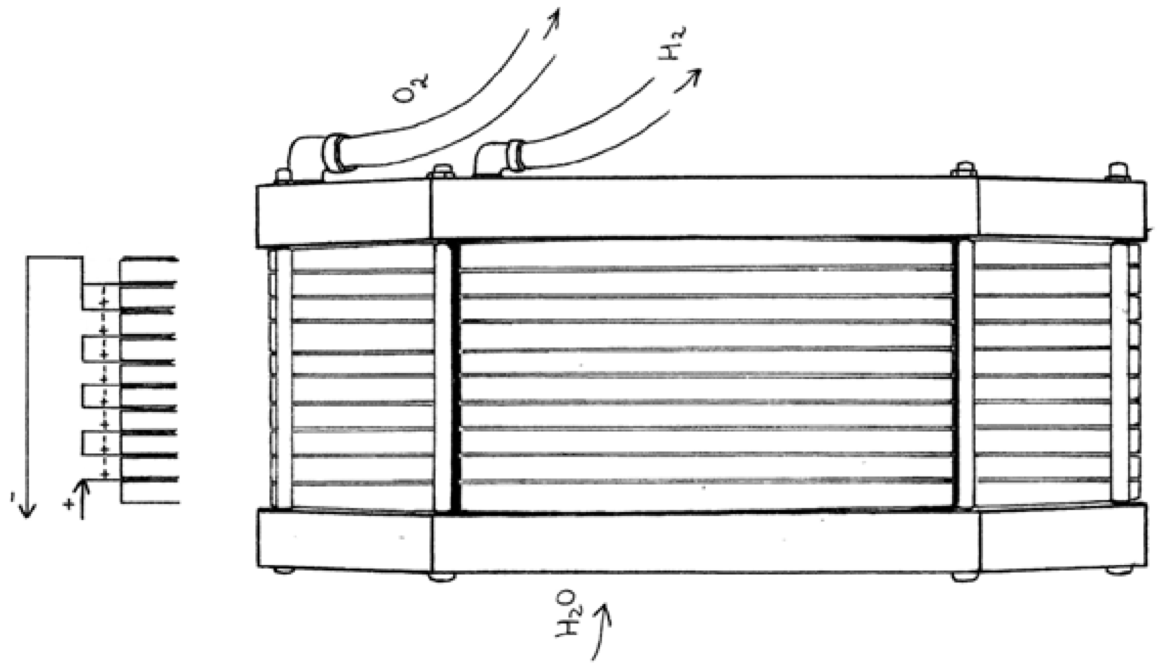

Figure 4 - Representation of Alkaline Water Electrolysis cells, with a total of 10 stacks (author)

The Alkaline Water Electrolysis follows the basic principle of a normal electrolysis, the main difference being the use of salts as catalysts and the use of higher temperatures/pressures, increasing its performance and efficiency, since water molecules are more easily split if more thermal energy is supplied, and the use of high pressures eliminates the need of mechanical compression of hydrogen, thus increasing its energy efficiency.

The main disadvantage of this process is the corrosive effect that the liquid electrolyte has on the equipment when it operates at high temperatures. This means that under these conditions the lifetime of the electrodes is short and so requires replacement, increasing the equipment cost. Besides the electrolytes, as mentioned before, the equipment is very resistant and can work for long periods.

Some alternative materials have been tested such as potassium titanate (K_2TiO_3) and politetrafluoroethylene (PTFE), polysulfone, asbestos coated with polysulfone and polyphenilene sulfide[17]. The corrosion rate should be taken into account since the characteristics of the electrolyte (for instance, if the temperature of the electrolyte is increased for efficiency) may corrode the material.

A gas-tight diaphragm is used to keep the H_2 and O_2 that is produced in the cathode and anode separated, since a physical barrier will avoid any form of mixture and promotes the greater purity of the products. The diaphragm is a barrier with pores of reduced sizes (1 μ m) that allow the transport of hydroxyl ions and water through but prevent the transportation of any gases. This is necessary because the Alkaline Water Electrolyzers use aqueous electrolytes, unlike certain electrolysis technologies that use a solid electrolyte membrane, which works as a diaphragm.

In terms of material, the most used diaphragm in alkaline electrolysis cells has been porous white asbestos ($Mg_3Si_2O_5(OH)$) however, being toxic for humans (due to its link between fiber exposure and lung diseases), other materials are preferred, either ceramic or microporous based[19].

Studies show that Alkaline electrolyzers connected to RES such as solar plants or wind farms are profitable[20], and by 2025 the growth of the use of RES and the improvement of electrolysis technologies is expected to further improve gains.

2.2.5.2. Polymer Electrolyte Membrane Electrolysis

The Polymer Electrolyte Membrane Electrolysis is an electrolysis technology that uses solid polymer membranes as electrolytes (Solid Polymer Electrolyte, SPE), promoting the separation of molecules and the conduction of protons (figure 5). This concept was first developed in 1960s to overcome the disadvantages of the Alkaline Water Electrolysis, by the use of a solid sulfonated polystyrene membrane as an electrolyte - a Proton Exchange Membrane or Polymer Electrolyte Membrane (both having the acronym PEM). A less common term for the membrane is Solid Polymer Electrolyte (SPE).

The use of polymer membranes in electrolysis has many positive aspects, mainly the high proton conductivity which improves the electrolysis chemical reactions, the low gas crossover rate which improves the hydrogen purity, and the possibility of operating at very high pressures.

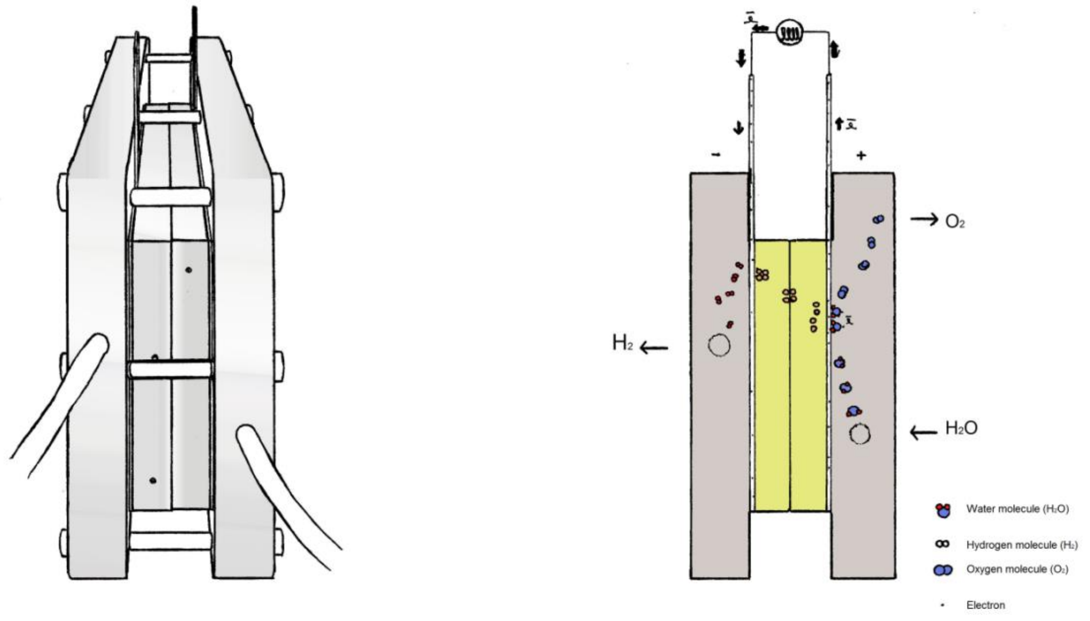

Figure 5 - Representation of a single PEM electrolyzer cell and its diagram, showing the basic principles of its technology (author)

Since the proton-conducting membrane is what distinguishes PEM electrolysis from the other technologies, it plays an important role in the hydrogen production and overall durability of the system. Due to their best performance, PFSA polymer membranes are used as solid electrolytes. These membranes excel due to their high chemical and thermal stability, as well as high mechanical strength and proton conductivity.

There are advantages in the use of PEM electrolyzers, mostly in the cost reduction associated with the use of higher current densities. Most electrolyzers work at low current density, which is around 0.2 A/cm^2, in order to achieve greater yields. If a higher current density is used, the required surface area and materials are reduced which means the equipment cost is decreased.

There are other advantages in the use of PEM electrolyzers, such as the decrease of ohmic loss caused by the electron flow in the electrodes and protons in the electrolyte. The decrease of the ohmic losses is possible due to the use of high pressures on very thin membranes (range 100-200 μm), unlike the alkaline electrolyzers. The high pressures can be achieved due to the physical properties of the electrolyte[21]. Some PEM electrolyzers have reportedly operated at pressures as high as 5000 PSI (350 bar)[22]. The process of compression of hydrogen during the electrolysis can be compared to an isothermal compression.

The PEM electrolysers also show high hydrogen purity due to the effective gas separation by the solid polymer membrane. The polymer characteristics are responsible for a low gas crossover rate. This is because there is a quick proton transport in the membrane, unlike other electrolysis technologies where the protons are delayed by inertia from the liquid electrolytes caused by its viscosity[23]. The volume of gas at the electrodes is reduced (gaseous phase) which improves product gas removal. The pressure increase also mitigates the damage of the membrane, caused by expansion and dehydration.

There are drawbacks associated with the use of these membranes, mainly because of their cost (400$ per square meter), the presence of fluorine in their structure (fluoride emissions cause degradation of the membrane)[6] and their mechanical strength loss at high temperatures (temperatures above 80ºC cause chemical degradation of the membrane)[7].

Like the Alkaline Water Electrolysis, this technology cannot use sea water because of its corrosive effect on the electrodes.

Table 2: Comparison between Alkaline Water Electrolysis and PEM Electrolysis

Alkaline Water Electrolysis	PEM Electrolysis
Advantages	
Advanced technology	High current densities
Low cost	Rapid system response
Long-term stability	Dynamic operation
Cost effective	High gas purity
Stacks in the MW range	High voltage efficiency
Simple catalysts (non-noble)	Compact system design
Disadvantages	
Low current density	High-cost components
Low operational pressures	Acid corrosive environment
Crossover of gases (decreased purity)	Possibly low durability
Low partial load range	Stacks below MW range
Corrosive liquid electrolyte	
Low dynamics	

2.3. Process of electrolysis and water

The process of water electrolysis requires a relatively large amount of water to produce industrial quantities of hydrogen. As such it is necessary to ensure there is a source of water available, which can either come from the sea, from the public water supply or as a waste from industrial processes.

The use of sea water in electrolysis has been widely discussed and researched. Sea water is rich in dissolved salts (a percentage of 3.5%), mostly Sodium (Na) and Chlorine (Cl). Those compounds make up for most of the dissolved salts in sea water, where Chlorine and Sodium have a concentration of 18980 ppm and 10561 ppm, respectively (table 3). This large concentration of ions could be useful for direct use in electrolysis, as it favors electric conduction. However, the presence of chlorine ions can corrode the equipment, usually by the formation of deposits and chlorine ion production from the electrical current that is applied to the electrolytic solution[24]. Chlorine ion production occurs whenever chlorine reacts with electrons. The Cl^- then competes with the OER in the anodic reaction of the Alkaline Water Electrolysis[25], in a reaction called Chlorine Evolution Reaction (CER), reducing the overall efficiency of hydrogen production and causing the formation of large amounts of hypochlorite formation (OCl^-) as follows:

$$Cl^-(aq) + 2OH^-(aq) \rightarrow OCl^-(aq) + 2e^- \quad (22)$$

There are different reactions through which Cl^- ions corrode the metal catalysts (M):

Adsorption of Cl^- by surface polarization:

$$M + Cl^{-} \rightarrow MCl_{ads} + e^{-} \qquad (23)$$

Dissolution by further coordination:

$$MCl_{ads} + Cl^{-} \rightarrow MCl_{x} \qquad (24)$$

Conversion from chloride to hydroxide:

$$MCl_{x}^{-} + OH^{-} \rightarrow M(OH)_{x} + Cl^{-} \qquad (25)$$

Therefore, if seawater is used, it is either subjected to a desalination process (later to produce a saline solution of KOH or NaOH) or the seawater is utilized directly by utilizing strategies for mitigating the equipment damage, such as coating the electrodes with a solution to prevent corrosion[26]. So the question arises: is it viable to use seawater in electrolysis?

Table 3: Composition of sea water[3]

Element	Chemical formula	Concentration (part per million)
Chloride ions	Cl^{-}	18,980
Sodium ions	Na^{+}	10,561
Magnesium ions	Mg^{2+}	1,272
Sulfur ions	SO_4^{2-}	884
Calcium ions	Ca^{2+}	400
Potassium ions	K^{+}	380
Bromine ions	Br^{-}	65
Carbon ions (inorganic)	CO_3^{2-},HCO_2^{1-}	28
Strontium ions	Sr^{2+}	13
Silicon ions	$HSiO_4^{1-}$	7.0-0.01
Boron ions	$H_2BO_3^{1-}$	4.6
Carbon (organic)	varies	3.0-1.2
Aluminum ions	Al^{3+}	1.9-0.16
Fluorine ions	F^{-}	1.4

As of today, desalination is a very viable option from a technological point of view. There are several mature desalination technologies widely used in large scale, such as distillation and reverse osmosis. The removal of impurities ensures that the electrodes won't be damaged by contact with the water and so the electrolysis process can be used without having equipment damage. There are disadvantages over using these technologies, mainly the economic impact they may cause due to the equipment investment cost and because electricity is required for the desalination technologies (electric power is necessary for heating in the case of distillation, or to compress the water if reverse osmosis is used). However, these technologies have been improved and the electricity consumption has been reduced while the desalination processes have shown greater efficiencies[27].

From an economical point of view it has been shown that the electricity demand to desalinate water are very low when compared to the actual process of electrolysis[28] and the cost of producing 1kg of desalinated water is much lower than the cost of producing 1kg of hydrogen. The reason for this difference comes from the requirements of the water electrolysis process, being a more complex process when compared to desalination. Water electrolysis has higher thermodynamic energy requirements, higher energy consumption and higher equipment costs. It has also been shown that the use of desalinated sea water for electrolysis is low compared to the consumption of desalinated water in general[28]. Even when considering a fully established green hydrogen economy its water requirements would be much lower than the globally desalinated water consumption.

The direct use of sea water for electrolysis has advantages, however there is limited research[29], and so as expected there are not industrial scale sea water electrolysers. Brine electrolysis is possible and seems to be promising due to the fact that it eliminates the need to desalinate sea water or use water from the public water supply and doesn't produce undesirable by-products from desalination technologies, such as waste brine. While studies have shown that it is not economically viable to develop a large scale electrolyzer plant that uses sea water at the present moment[7,30], there is research regarding this type of electrolysis technology that tackles the main problems associated with using seawater[31].

It has been demonstrated that the electrolyzer cells lose activity if seawater is present, as chlorine ions reduce the transportation of OH^- across the membrane[32]. This is problematic since it decreases the performance of the electrolyzers. Curiously, it has been shown that cell power performance is recovered if the electrolysis process comes to a halt and the electric potential is later re-applied (in 100 hours, a recovery effect was observed after 10 minutes, and then 1 hour)[32]. Such measure may be useful if intermittent energy sources, such as solar PV, are used to power the electrolyzers.

A promising solution uses a transition metal nitride electrocatalyst[33], which is corrosion-resistant, electrically conductive and mechanically resistant material that allows the use of sea water, since the electrocatalyst prevents the CER. The nitride electrocatalyst not only prevents the corrosion of equipment, but it was also shown to be more efficient than the usual platinum electrocatalysts.

One proposed solution involves the coating of the electrolytes with a protective layer, such as iridium oxide/titanium coat, which work on very low current densities to mitigate the chlorine evolution reaction. This measure was shown to greatly reduce the damage. A similar solution is proposed where the electrodes are covered with nickel phosphide, promoting nickel cobalt nitride growth, where the advantages are threefold: both compounds are highly conductive which improves the hydrogen splitting reaction kinetics, the nickel phosphide microsheets provide a large surface area of active sites, and the microsheets are anticorrosive, allowing for seawater to be used[34].

Another solution involves the use of desalination membranes that cover the electrodes, thus preventing damage by contact with sea water. In this method the membranes that were used are called *forward osmosis-water splitting* (FOWS) cells, which promote the direct desalination of sea water through the forward osmosis process (figure 6)[35]. This interesting solution was performed at an applied current of 250 mA, 2.8 V, in a saltwater environment over 48 hours. Results showed an effective electrolysis with only a small salt accumulation in the electrodes.

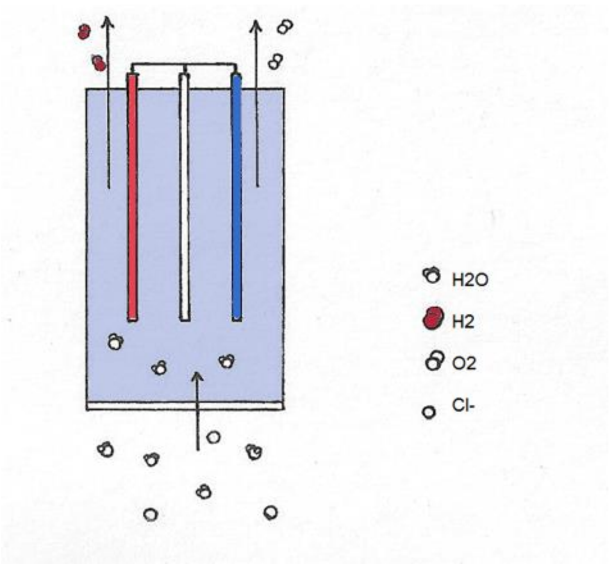

Figure 6 – Working principle of a FOWS cell (author)

The use of asymmetric electrolytes, which consists on the use of a different electrolyte for the anode and cathode, improves the performance of the electrolyzer since it prevents the seawater from increasing the pH of the electrolyte, due to the alkaline Cl^- activity[36].

These processes, although very promising, are still being researched and are not yet large-scale technologies. Currently, it is more viable to purify water through desalination, considering the large quantities of water that are usually needed for the electrolysis process. The desalination technologies will be discussed since there is very well-established data on their performance, advantages and disadvantages. Since there are a high number of desalination plants throughout the world it is possible to know their advantages and limitations, allowing for a comprehensive understanding of these technologies.

Finally, certain types of wastewaters could be used as a source for producing hydrogen through water electrolysis. There are studies that show wastewater can be used[37], however certain precautions must be taken (such as coating the electrodes with a solution) and there are not yet any large-scale water electrolysis plants that use wastewater as a water source.

There are several factors that should be considered when using such technologies, the most important being technological maturity, the possible implications and negative impacts of using the technology and its economic viability.

2.3.1. Desalination

2.3.1.1. Desalination technologies

The process of removing salt from water is relatively simple, regardless of the technology. Historically the method for removing salt from water has been distillation, which uses heat to evaporate the water and thus separating it from its dissolved salts. Newer technologies have been developed to the point of being industrially viable at relatively low energy costs.

There are two types of desalination technologies, which can be divided as thermal methods and membrane methods (table 4). The desalination technologies generally have several phases, common to each method: the water is sourced, and then supplied to a pre-treatment section and then to the desalination system, and finally the water is subjected to a post-treatment to improve quality. The brine that is a by-product of the desalination process is disposed, usually to the sea.

New technologies have been developed and so there are currently very efficient desalination methods, both thermal-based and membrane-based. Examples of thermal methods are Multi-stage Flash Distillation (MSFD), Multiple-effect Distillation (MED) and Solar Distillation. Examples of membrane methods are Reverse Osmosis (RO) and Electrodialysis (ED).

Table 4: Main desalination technologies

Thermal-based	Multi-stage Flash Distillation (MSFD) Multiple-effect Distillation (MED) Solar Still Distillation (SSD)
Membrane-based	Reverse Osmosis (RO) Electrodialysis (ED)

Thermal-based desalination methods rely on the evaporation of water, producing water vapor, which is then condensed. The heat for the evaporation of water is usually generated from a thermal process such as fuel combustion or waste heat. The most efficient thermal technology is MSFD[38].

Membrane-based desalination methods rely on the filtration of water using semipermeable membranes, which are permeable to water molecules but not dissolved salts. The sea water is pressurized in some methods, such as RO to force the water through the membrane. The most efficient membrane technology is RO[38].

The electrical energy required for MSFD and RO is similar; however MSFD also requires thermal energy which increases the electricity needed, unless the MSFD unit is coupled in a CHP system. This means that between the two technologies MSFD may require the most energy. However, MSFD can produce water in higher quantities, compared to RO (table 5).

Table 5: Comparison between MSFD and RO technologies

Technology	**Average capacity [m^3/day]**	**Electricity consumption [kWh/m^3]**	**Thermal energy consumption [KJ/kg]**	**Water pressure [atm]**	**Water cost [€/m^3]**
MSFD	23000-528000[39]	4-6	190-390	0.01-1[40,41]	0.48-1.49[41]
RO	1000-320000[41]	3-5.5	-	54-67[42]	0.06-1.46[41]

Since MSFD and RO are currently the most efficient desalination methods, these technologies will be discussed in this dissertation to better understand the viability of their use in this project.

2.3.1.2. Multi-stage Flash Distillation

The first multi-stage flash distillation plant was established in the 1950s by the Weirs of Cathcart, an engineering firm in Scotland, and in the following decades it was popularized, becoming the most used desalination method[43].

The MSFD technology follows the basic principle of distillation: saline water is heated to the point where it starts to boil, forming water vapor, and so freshwater is collected after the water vapor condenses. Distillation is a very old process; however the MSFD technology is far more efficient than a simple distillation unit, as it increases its yield through the use of decreased pressures and several flash stages.

The MSFD process has several stages (figure 7), and it can be divided in two sections – a brine heater section, where the sea water is heated from an external supply, and a heat recovery section, where thermal energy is recovered from the process to pre-heat the sea water. As it is necessary to heat the saline feed water, the thermal energy may be obtained through fuel combustion or by using waste heat from an industrial plant.

Initially the saline water is used as a cooler for the condenser and after a gradual temperature increase fresh water is produced. As the saline water enters the flash stages it starts to evaporate, since it was heated in the heat exchanger, allowing for the collection of fresh water. The brine that is accumulated from each stage is disposed to the sea.

The MSFD units normally have several flash stages (ranging from 15 to 25 depending on the unit size) to increase efficiency. This is because the internal pressure of each stage drops, due to the use of steam ejectors or vacuum pumps that remove steam from the flash units, which in turn lowers the boiling point of the saline water. As the heated saline water enters the flash stage, it rapidly vaporizes due to the low pressure causing the “flashing effect”, since the water quickly flashes into steam[44].

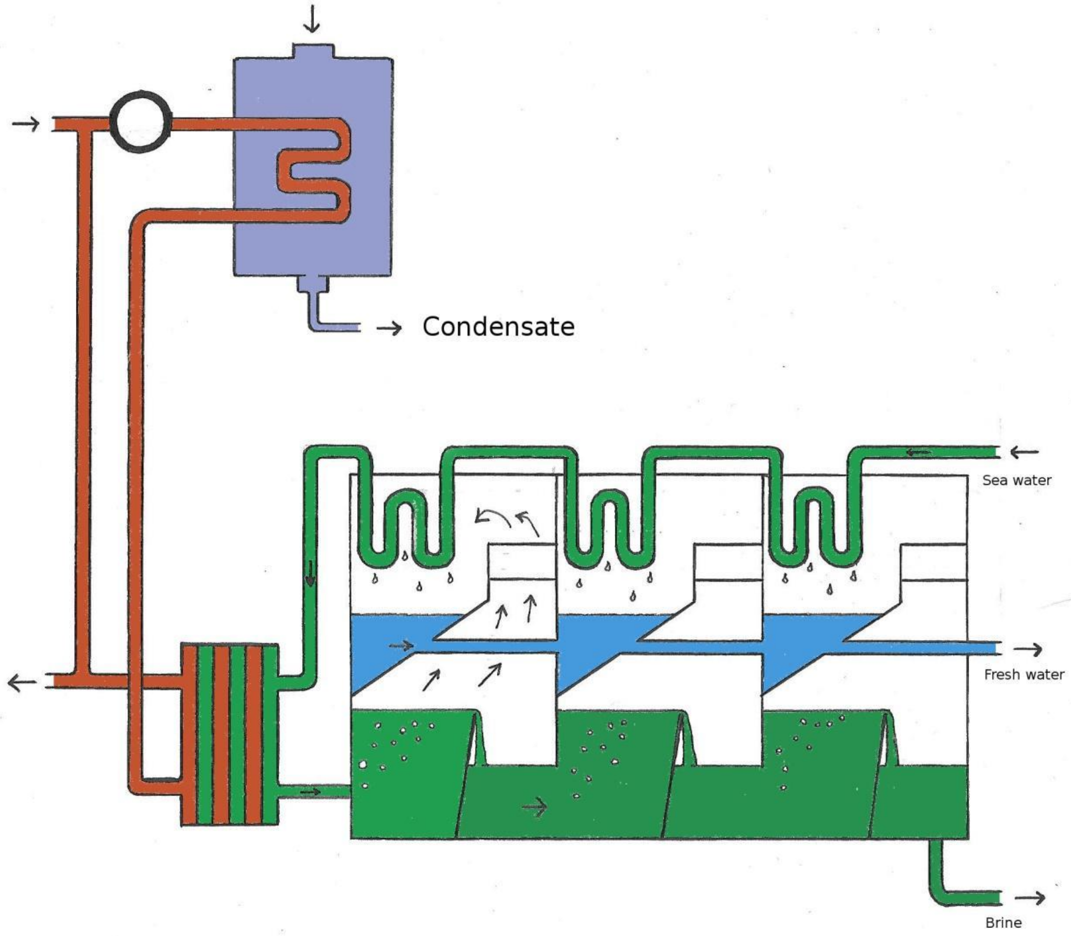

Figure 7 – Diagram of a Multi-stage Flash Distillation (MSFD) process, based on a WÄRTSILÄ MSF evaporator (author)

Only a small percentage of the heated saline water turns into water vapor, depending on the pressure of the stage. The generated vapor condenses, forming fresh water, a process that goes on until the saline water cools to the point where it stops vaporizing. The temperature range of the MSFD units is 90ºC-110ºC[45].

There have been improvements to this technology to increase efficiency. One of such has been the introduction of a heat rejection made of two to three stages, where saltwater is used for cooling. Brine and freshwater are produced in these stages. After this process a part of the saline water is discharged while the rest is mixed with part of the brine formed in the second or third flash stage and sent to the main unit, where it is heated in the brine heater before entering the flash stages. Once in the flash stages, the saline water starts to condensate, where more freshwater is produced (figure 8). Desalination plants with this technique have 4-40 flash stages[42] and 2-3 heat rejection stages.

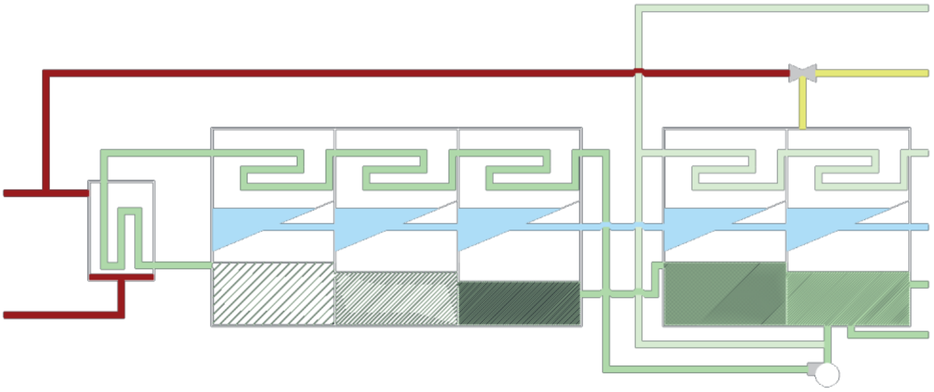

Figure 8 – Diagram of an improved MSFD unit (author)

There have also been other improvements to this technology, such as the introduction of anti-scaling chemicals in the water to prevent the formation of limescale on the equipment (calcium carbonate deposits that often form in the surface of equipment), as well as better automation and equipment for the desalination units[46].

The capacity of a MSFD unit varies, however the average numbers range 4000-528000 m^3/day[39, 46], depending on whether it is a small- or large-scale desalination plant.

Advantages and disadvantages of the MSFD technology:

Advantages

- MSFD plants are relatively easy to install and operate;
- The water normally has a very low dissolved solids value (averaging 5 ppm), which reflects in a very high level of purification[46];

Disadvantages

- The MSFD can operate at temperatures higher than 115ºC for increased yields, however such high temperatures cause scaling problems[46];
- The addition of stages increases efficiency and quantity of water produced, however this in turn increases costs and the complexity of the desalination plant[46];
- A problem common to other desalination methods is the disposal of brine, as it can disrupt the sea ecosystems if it is discharged to the sea;

2.3.1.3. Reverse Osmosis

The reverse osmosis process uses semipermeable membranes to separate dissolved salts from water. Its principle, as the name suggests, is the opposite of osmosis. Osmosis is the spontaneous movement of the solvent (such as water) of a more diluted solution to a more concentrated solution (with more solute or dissolved salts), through a semipermeable membrane to balance the energy potential of both solutions. This phenomenon is observed in nature, namely in cells, since water is essential for their biological processes. In RO the solvent is forced through the semipermeable membrane by applying pressure which produces a more diluted solution (fresh water), as well as a higher concentrated solution (brine) due to the increase in the concentration of solutes (figure 9). Since the membrane is only permeable to water, the fresh water is separated from the brine. This is achieved if the applied pressure is greater than the osmotic pressure.

The osmotic pressure (π) of sea water is high, normally between 24 to 32 atm (for a NaCl concentration range of 3-4%), and so the applied pressure (P) has to be higher in order counter the osmotic pressure ($\Delta P > \Delta \pi$)[47]. This value can be obtained from the Van't Hoff's equation, which is the following:

$$Posm = i[c]RT \qquad (26)$$

Where,

- *i* is the van't Hoff index (dimensionless value), which accounts for the number of particles that are active in the osmosis process, that is given by $i = 1 + e\ (v - 1)$, where e is the degree of solute molecules that are dissociated, and v is the number of ions formed by the dissociation. In the case of sodium chloride, $i = 2$ ($e \cong 1$, $v = 2$);
- *[c]* is the molar concentration of the solute;
- *R* is the ideal gas constant (equal to 8,31441 J K^{-1} mol^{-1});
- *T* is the absolute temperature of the solution;

Considering that the salt concentration of saline water ranges 0,51-068 mol L^{-1} (3% to 4%)[18], at a temperature of 25ºC the osmotic pressure of saline water ranges between 24,6 atm and 32,5 atm.

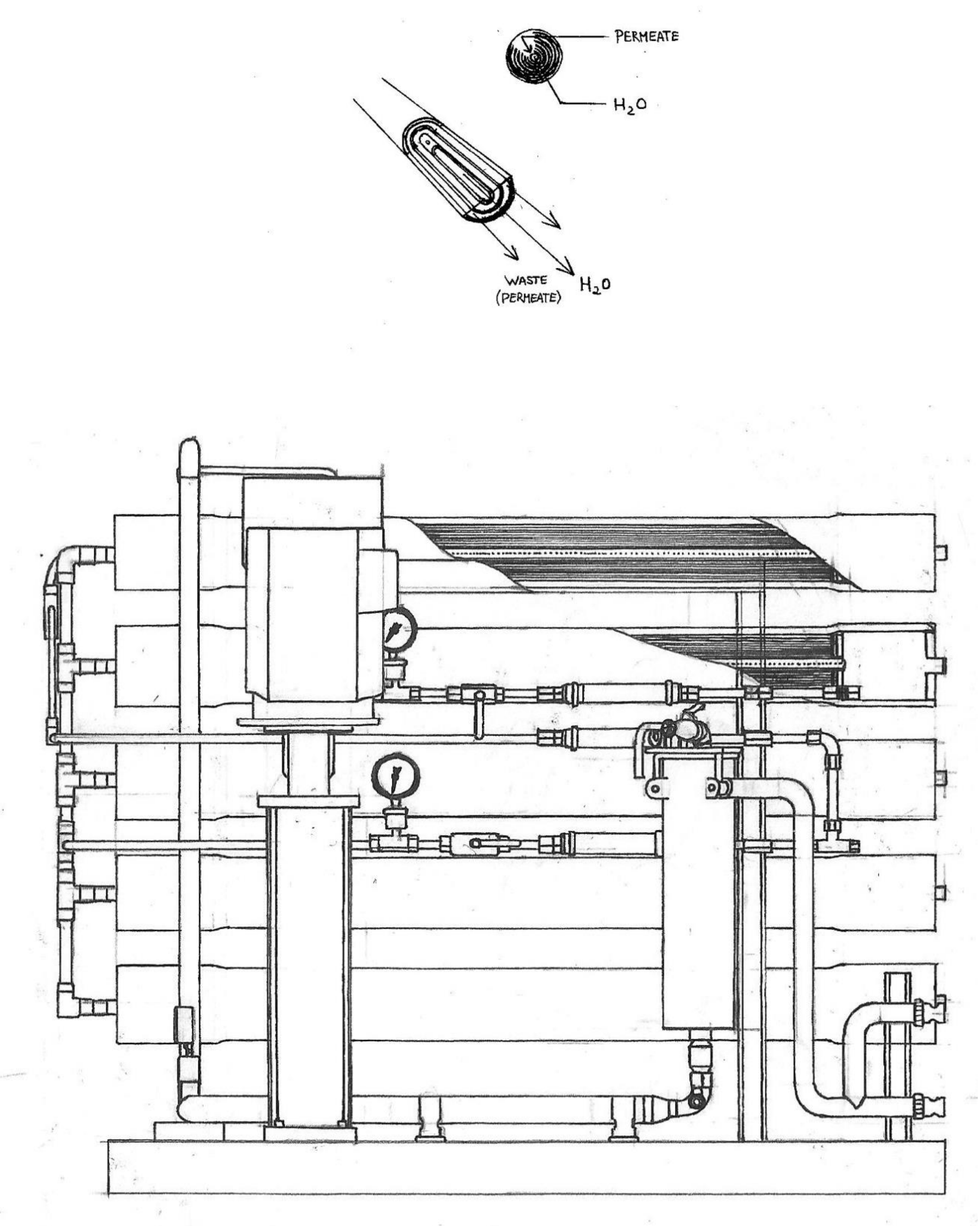

Figure 9 – Diagram of an S-800 Spiral Reverse Osmosis (RO) system showing a section of the membrane filters (author)

The RO starts with the removal of solid particles of the saline water, in a process called pre-treatment. The pre-treatment is necessary since the RO pressure vessels (where the semipermeable membranes are found) normally have a small diameter, which means that large solid particles cannot be present in the saline water. After the pre-treatment, the saline water is pressurized before entering the semipermeable membranes.

In order to achieve a high pressure the RO unit requires a source of energy, either electrical or mechanical, to pump the saline water to the semipermeable membrane (pressurized by a High Pressure Pump, or HPP).

Due to the process efficiency, only a part of the saline water becomes fresh water. The percentage of fresh water that is obtained can be calculated using the Recovery Ratio (RR), which is defined as the ratio between the freshwater flow (*Qf*) and the saline water flow (*Qs*). RR normally has values between 35% and 50%. The saline water that is not converted to freshwater is discharged as brine. A simple diagram of the RO is shown in figure 10.

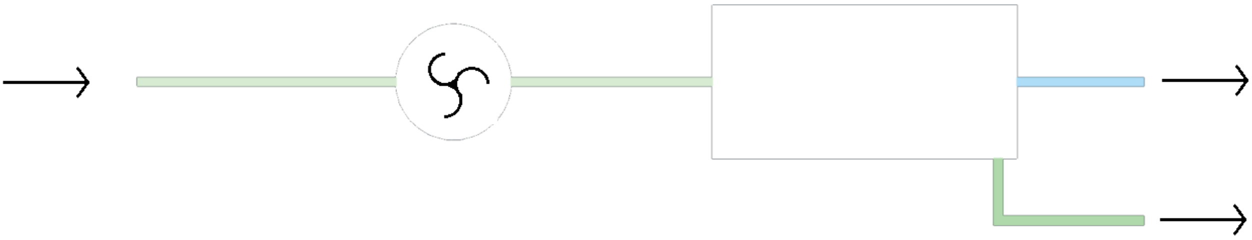

Figure 10 – Diagram of a simple RO unit

Several technologies have been proposed to increase the energy efficiency of the RO systems. One of such was the introduction of a Pelton turbine (centrifugal device) to recover energy from the brine that is expelled by the pressure vessels. The brine flow has a high energy potential since its pressure drop is very low, only about 2-3 atm[48]. The energy recovered by the Pelton turbine from the brine flow is transferred to the HPP. An electrical motor is also included to increase the HPP performance (figure 11).

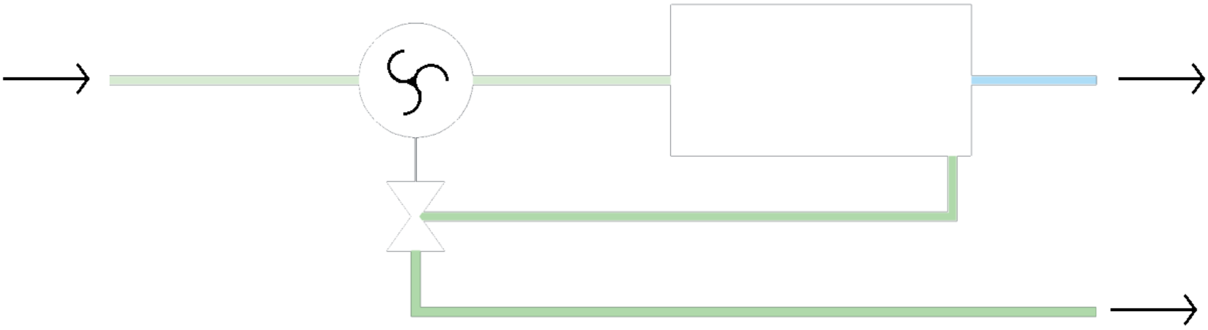

Figure 11 – Diagram of a RO unit with a Pelton turbine and an electrical motor (author)

Another proposal has been the introduction of another centrifugal device, a turbocharger (turbine) that increases the pressure of the saline water flow. This means the saline water is pressurized two times: firstly it is pressurized by the HPP and secondly by the turbocharger. Part of the brine flow is discharged by the turbocharger while the rest increases the efficiency of the Pelton turbine, which reduces the energy demand of the HPP. This proposal is shown to be even more efficient than the previous one, since the saline water flow is pressurized twice, lowering the energy costs.

Other ways of improving this system have been proposed, such as the introduction of an electric motor on the turbocharger system to control the saline water flow pressure more efficiently, showing high pressure boosts (proposed by the Fluid Equipment Development Company, FEDCO)[49].

Another solution which uses Isobaric Devices has been proposed. The main concept of using an isobaric device is to increase part of the saline water pressure using the discharged brine's pressure. These devices, also called isobaric pressure exchangers, transfer a part of the brine's pressure to the saline feed water without mixing the two fluids to a noticeable level.

One of such devices is the Rotary Pressure Exchanger (RPX). The saline water enters one end of the cylindrical rotor while pressurized brine enters the other end (pistons at the middle prevent mixing). This causes the pressurized brine to push the saline water forth, increasing its pressure, without mixing. The RPX not only works using horizontal movement but also rotational movement. The rotational motion is known to increase the pressure transfer in the RPX, since it has been observed that the pressure of the saline feed water is nearly the same as the brine. Due to the efficiency in transferring the brine pressure to the saline water, this device greatly lowers the electrical costs of the desalination unit.

Advantages and disadvantages of the RO technology:

Advantages

- The electricity costs are generally lower than other desalination technologies;
- The development of energy recovering devices has greatly improved the efficiency of the RO units, allowing for an effective pressure transfer from brine to the saline water;
- Membranes are durable and relatively cheap, decreasing the economic costs;
- There are less corrosion problems when compared to other desalination technologies due to less use of metal equipment and to an efficient control of ambient temperature;

Disadvantages

- The saline water requires pre-treatment in order to remove particles that may interrupt the water flow, increasing the operational costs;
- Even though scaling is not as common to RO as it is to other desalination technologies, it is still problematic and causes equipment damage, increasing maintenance costs;
- Brine disposal can be a major issue if it is discharged to the sea, posing risks for the marine ecosystems, a problem common to the other desalination technologies. The disposal of brine on land is also problematic as it can damage the soil;

3. Methods

3.1. Energy modelling and calculations

Energy modeling consists of building mathematical models to simulate and analyze energy systems. Modeling is important for engineering systems and energy policy, allowing the determination of the overall feasibility of projects, including costs, emissions and the efficiency of the system. EnergyPLAN is one of such energy modeling tools, and it will be used and discussed in this dissertation.

EnergyPLAN is an energy modeling software developed and continuously updated by the Sustainable Energy Planning Research Group at the Aalborg University in Denmark, available worldwide for download. It can simulate the operation of an entire national energy system, giving hourly values of several sectors including electricity, industry, transport, heating, and cooling. The EnergyPLAN software simulations can go from an entire national grid to a small-scale unit, depending on what is specified (figure 12).

In order to simulate a system, parameters have to be specified. For example, if an energy system is being simulated, energy demand (such as electricity demand, fuel consumption or freshwater demand) must be specified. If the energy system has energy sources, such as wind, nuclear or wave power, its capacities also need to be supplied.

In this dissertation the EnergyPLAN software will be used to simulate the operation of a hydrogen production plant, the associated desalination system and to estimate the quantities of water produced by the electrolysers, the amount of energy required for the desalination process and the water storage capacity for the desalination. The values of these parameters differ for each established scenario.

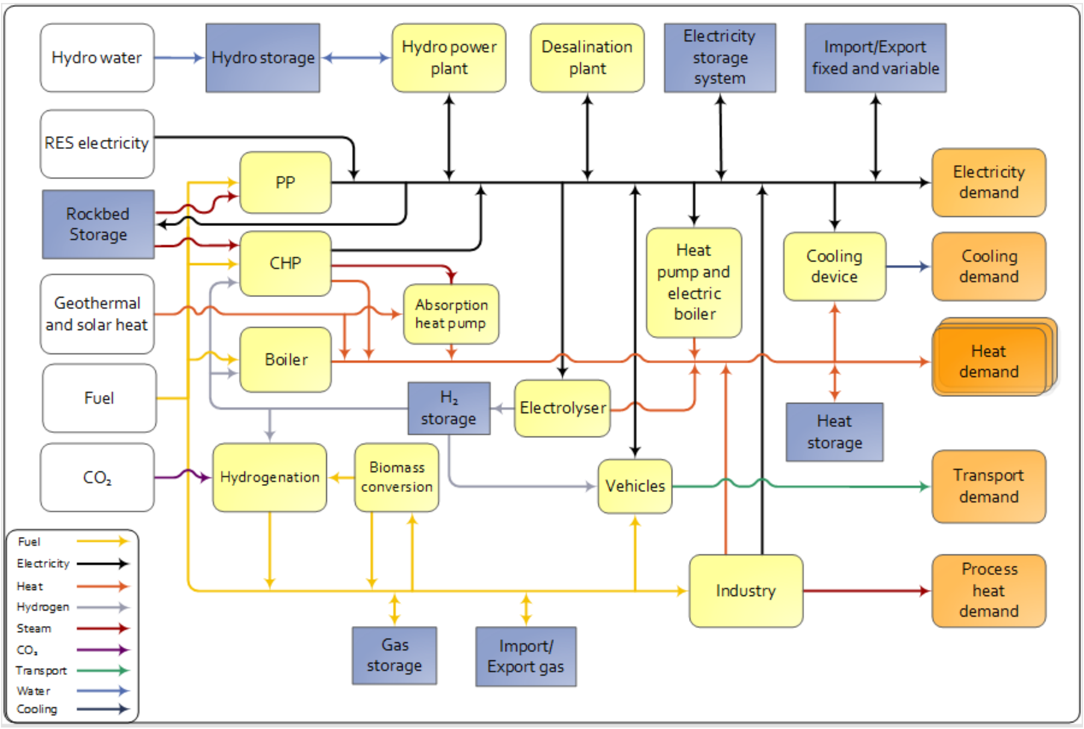

Figure 12 – Overview of the EnergyPLAN system

3.2.1. Hydrogen production scenarios and desalination unit

The work we present here expands the scope of the analysis performed in a masters dissertation by F. Franco[50], that explored the main features of a GW-scale hydrogen production facility with regards to hydrogen yield and the levelized cost of hydrogen (LCOH).

In that work the operation of the hydrogen plant is simulated by considering different weather conditions and plant configurations. While different, the scenarios have a few common features. The electrolyzer electric input power ranges from 1 GW to 3 GW and the energy is supplied by either solar PV panels, wind turbines, or a combination of both, whose capacity can range from 1 GW to 3 GW. The system can either consume or inject electricity on the national electricity grid, depending on the operation mode. The feedstock water was considered to be supplied by the local grid and the main focus of the study was on its contribution to the levelized cost of hydrogen.

Different weather conditions have also been considered, to better analyze the RES performance. Since there is data regarding the performance of solar PV and wind energy from 2011 to 2019, it was possible to conclude that 2012 is a sunny year, with higher solar PV energy production, and 2016 is a windy year, with higher wind energy production.

Two main inputs are vital for the functioning of the hydrogen production plant: energy and water (figure 13). The energy can either be sourced from the grid or it can be produced, or in certain cases it may come from those two sources, and the water can either be sourced from the public water supply or from desalination. If desalination is used, it is necessary to provide energy for the process. In periods of severe drought, the desalinated water could be injected to the public water supply, if hydrogen production is halted.

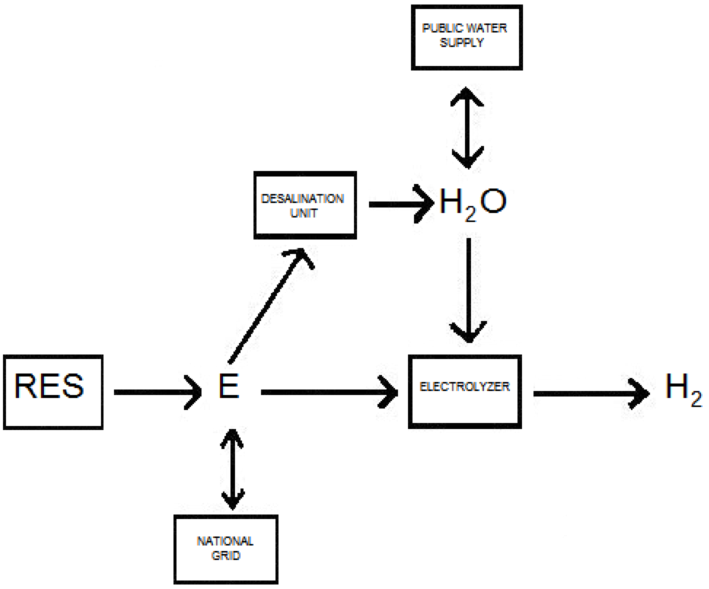

Figure 13 – Diagram of the hydrogen production facility and desalination unit

Operating mode A – hydrogen production in a constant regime

In this mode, the electrolyzer load – the amount of electricity that is consumed for the electrolysis process – assumes a constant value.

This means that there are energy exchanges with the national grid, depending on each specific case. There may be energy imports if the electrolyzer load is above the power generated by the RES. In other cases, there may be energy exports if the electrolyzer load is below the power generated by the RES. In order to maintain a neutral import balance, the electricity imports and exports are set to have the same value.

The RES used on each case varies, as well as its power. The electrolyzer power will also vary, and the yearly weather conditions are either set to be sunny or windy. Therefore, the import/export values depend on the RES, the electrolyzer load and the weather (figure 14).

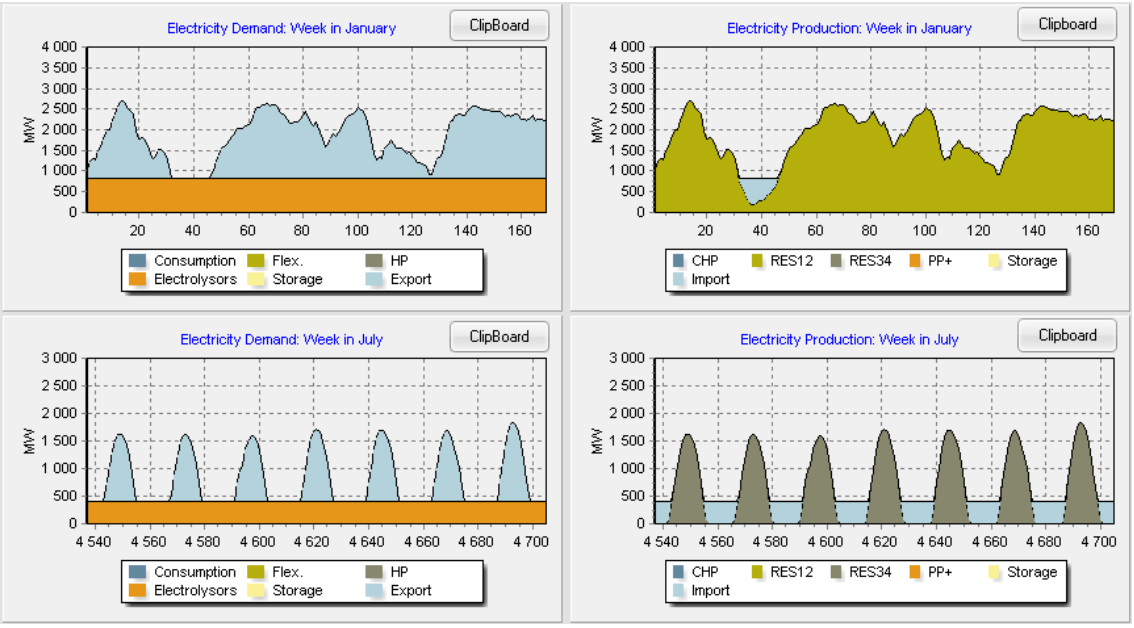

Figure 14 – Electricity demand (a) and electricity production (b) of wind power (windy year) and electricity demand (c) and electricity production (d) of solar PV (sunny year), in operating mode A. Both examples have optimal weather and the displayed months (January for wind power and July for solar PV) represent peaks of electricity production.

Operating mode B – Hydrogen production in a self-sufficiency regime with a single RES

In this mode, the energy required for the electrolyzers is provided only by either solar PV or wind power. This means that the system's electricity is provided by a single RES (figure 15).

This mode is not expected to withdraw electricity from the national grid to feed the electrolyzers. Therefore, there is hydrogen production if energy is being generated by the RES, and part of the energy will also supply the desalination unit. In case there is excess electricity, it will be injected to the national grid. In these cases, in order to avoid overcharging, the electrolyzers will work at a maximum of 50% above their nominal capacity, for shorts periods of time[50].

In case there is not enough electricity production, the electrolyzers and desalination units will not work.

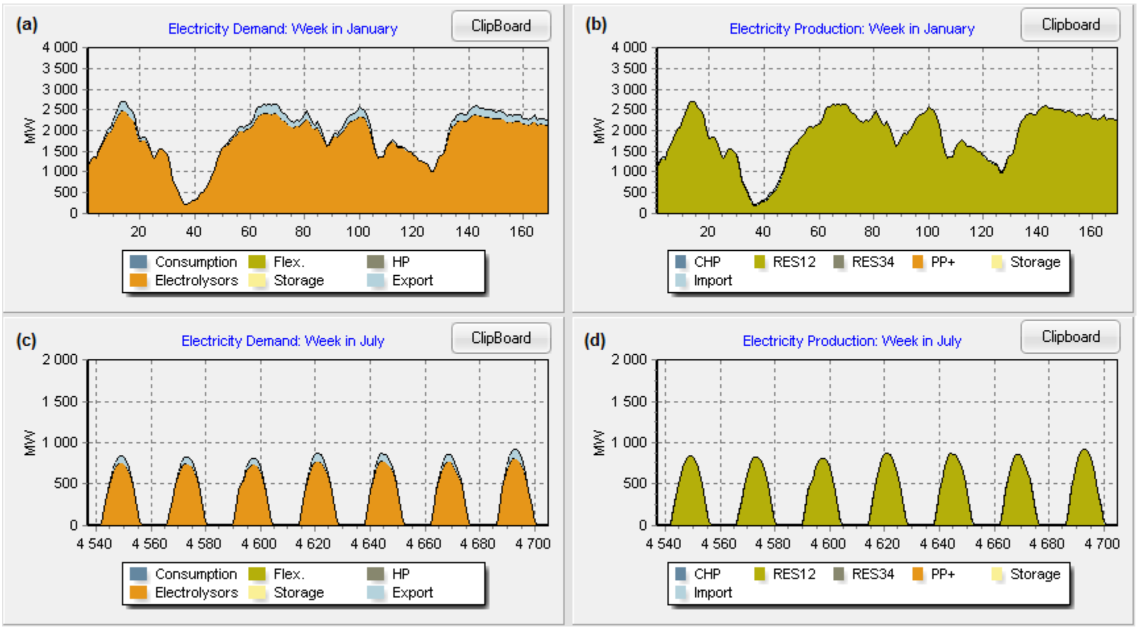

Figure 15 - Electricity demand (a) and electricity production (b) of wind power (windy year) and electricity demand (c) and electricity production (d) of solar PV (sunny year), in operating mode B.

Operating mode C – Hydrogen production in a self-sufficiency regime with a combination of RES

In this mode, the energy required for the electrolyzers is provided only by a combination of RES, solar PV and wind power.

This mode has the same specifications as mode B however the combination of RES makes the system less prone to intermittence, since the wind turbines are expected to work during the night when the solar panels aren't producing energy (figure 16).

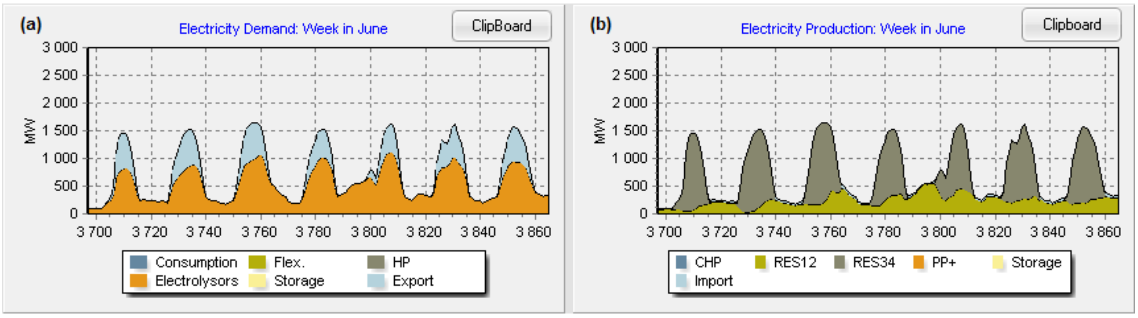

Figure 16 – Electricity demand (a) and electricity production (b) of wind power and solar PV (sunny year), in operating mode C. Because this mode combines two RES, the electricity production is continuous (no intermittence).

Operating mode D - Hydrogen production in a self-sufficiency regime with a single RES and a minimum electrolyzer load of 20% of nominal capacity

In this mode the electrolyzers work at a minimum load value of 20% of their nominal capacity. This means that the system will import energy from the national grid if the electricity production falls below the minimum required for the electrolyzer load.

The energy is produced by either solar PV or wind power. The desalination unit is powered either by the RES or the national grid, depending on the amount of energy that is generated. Like the other modes, the electrolyzers are restricted to work at a maximum load of 50% above their nominal capacity (figure 17).

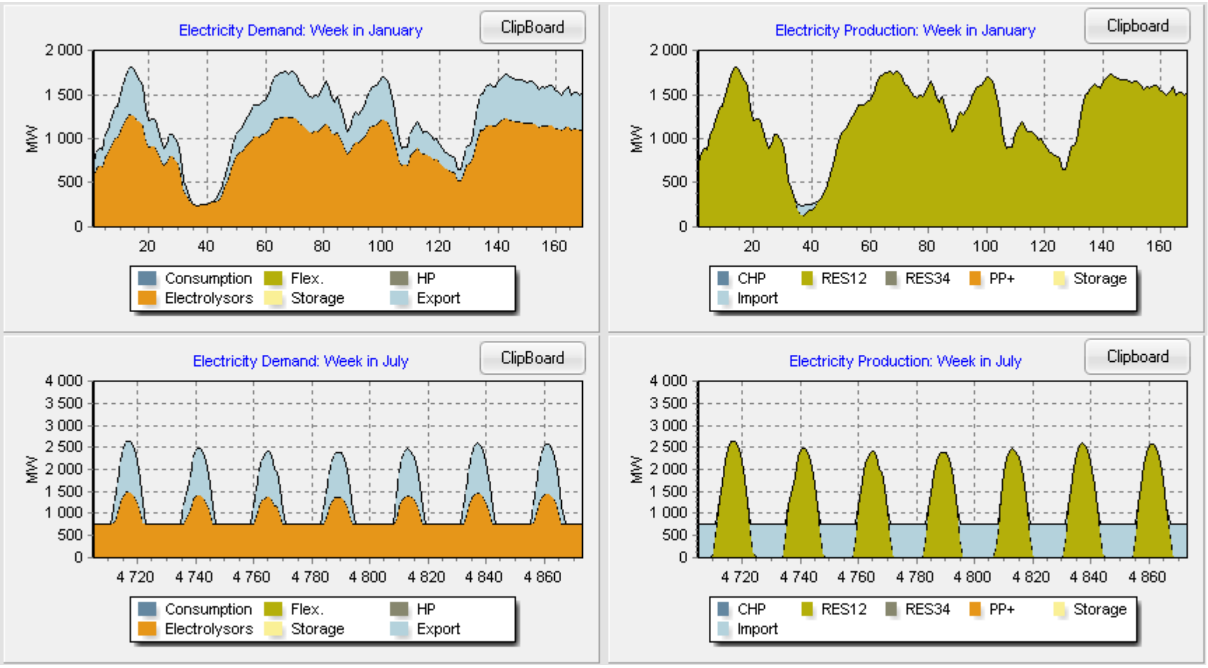

Figure 17 – Electricity demand (a) and electricity production (b) of wind power and electricity demand (c) and electricity production (d) of solar PV, in operating mode D. The electrolyzer load of 20% can be seen as a constant value.

Operating mode E – Hydrogen production in a self-sufficiency regime with a combination of RES and a minimum electrolyzer load of 20% of nominal capacity

This operating mode is similar to mode D, however a combination of RES is used instead of a single RES (figure 18).

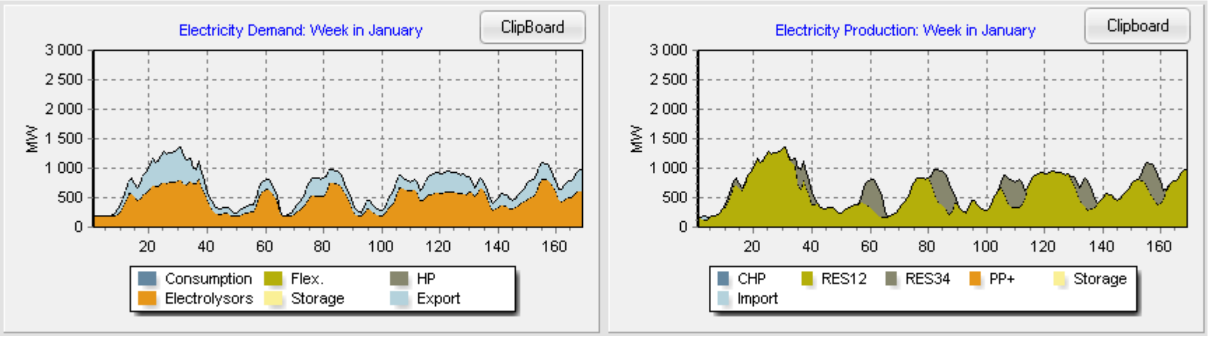

Figure 18 – Electricity demand (a) and electricity production (b) of wind power and solar PV (sunny year).

Since the process of water electrolysis requires freshwater, the introduction of a desalination unit to the system may be an advantageous and sustainable option to obtain large quantities of freshwater. Such addition reduces the pressure on local water resources, preventing water shortages.

The desalination unit is expected to use part of the energy generated by the RES, assuming not all the electricity is used to produce hydrogen. Ideally if the system is self-sufficient it will not withdraw energy from the national grid to supply the electrolyzers or desalination units.

The water storage unit should accommodate the electrolyzers water requirements for a certain amount of time, in case of an emergency.

The dissociation of the water molecule in the electrolyzer is not fully efficient and that should be taken in consideration for estimating the amounts of water necessary for the operation. By analyzing the characteristics of a number of commercial electrolyzers we determined that, on average (and only for the electrolyzers that were analyzed), the water consumption is double the stoichiometric amount necessary to produce a given quantity of H_2, that is, the water dissociation efficiency is 50%. In terms of quantities, the desalinator will have to provide 18 kg of water for each kg of hydrogen. Table 6 shows examples of efficiencies based on the electrolysis technology:

Table 6: Efficiency of electrolysis according to the technology

Technology	**Electrolysis efficiency**
Alkaline	71%[51]-73%[52]
PEM	56%[52]-63%[51]

The efficiency of 73% was used for the calculations, although with technological advances of the electrolysis technologies such numbers are only expected to increase.

3.2.2. Technical analysis

Each combination was simulated with different specifications to obtain data on the desalination and storage units. Such information allowed an accurate comparison of values to determine the energy implications of using desalination with and without storage. The minimum, maximum and average hourly values of water that the electrolyzers require were also calculated in order to determine the size of the storage facilities. Lastly the desalination plant capacity was also calculated.

A nomenclature was used to specify each of the combinations, according to its operating mode, weather condition, electrolyzer power and RES power. Figure 19 shows one example:

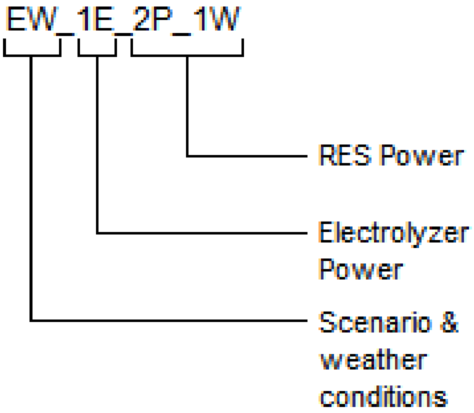

Figure 19 – Example of nomenclature of a combination

Figure 19 shows the nomenclature for the combination of mode E in a windy year (W), having an electrolyzer power of 1 GW (1E) and a RES power of 2 GW photovoltaic (2P) and 1 GW of wind power (1W). The nomenclature is shorter for combinations which only use one RES, such as BS_2E_3P (operation mode B in a sunny year with 2000 MW electrolyzer power and 3000 MW solar photovoltaic).

Of the 144 combinations that were designed[50], 4 were chosen. The choice of these combinations should be briefly discussed. One of the figures of merit for the system is total annual H_2 production and this value ranges between 35 and 190 kton for the 144 combinations[53]. Generally, combinations with larger electrolyzer and wind generation capacities are the ones that yield larger quantities of hydrogen annually, as wind power generally has larger equivalent full load hours. But total H_2 production cannot be the sole guide for making and investment as such production could reach prohibitive costs depending on the combination and size of the technologies employed. Therefore, another figure of merit must be taken into account. For that purpose the choice is “investment productivity”, i.e., the amount of hydrogen produced by each euro of investment, that for the 144 combinations ranges between 0.4 and 0.75 $kgH_2/€_{annualized\ costs}$[54]. In this case, it should be noted that the highest investment productivities are obtained for configurations with low electrolysis capacities and using solar PV power. These combinations generally yield low annual production values because solar PV has lower equivalent full load hours. Consequently, the best combinations are those that maximize the product *annual* H_2 *production x investment productivity*. For various values of discount rate a set of combinations consistently appears as the best options, as shown in Table 7. These are the four combinations that are analyzed below.

Table 7: Combinations that maximize the product *annual* H_2 *production x investment productivity* and their specifications

Discount rate		**Scenario/combination**	**Electrolyzer power (GW)**	**Wind power (GW)**	**Solar PV power (GW)**	**Exchanges with national grid**
Electrolyzer	**RES**					
3%	3%	Bs2E3P	2	0	3	No
		Cs1E2P1W	1	1	2	No
		Ew1E2P1W	1	1	2	Yes
6%	6%	Cs1E2P1W	1	1	2	No
		Ew1E2P1W	1	1	2	Yes
		Cw1E2P1W	1	1	2	No
3%	6%	Bs2E3P	2	0	3	No
		Cs1E2P1W	1	1	2	No
		Ew1E2P1W	1	1	2	Yes
3%	9%	Cs1E2P1W	1	1	2	No
		Ew1E2P1W	1	1	2	Yes
		Cw1E2P1W	1	1	2	No

The technical analysis will establish and relate the obtained results, namely the hydrogen that is set to be produced in one year as well as the amount of water necessary for the process, of each combination. The implications of desalination will be analyzed, which include the predicted size of the desalination plant and the energy necessary for it.

3.2.3. Economic analysis

The estimate of the main costs of the desalination unit and storage facilities was determined by several factors. Desalination plants throughout the world vary in size, technology and several other aspects. Therefore, for this estimate, similar examples of desalination plants will be considered.

For the economic analysis the investment costs of the desalination units and the storage unit are used. The desalination capex and opex will be used. Other variables, such as the discount and interest rate will also be used.

The discount rate of desalination is set to be 5%. The values for the discount rate, interest rate, specific Operation and Maintenance (O&M) and equipment lifetime were based on articles covering the economic evaluation of seawater desalination[57]. For the electrolyzer and RES technologies the values were adapted from the EU Reference Scenario. Table 8 shows the CAPEX and OPEX values of the electrolyzer and RES, in $€_{2015}$:

Table 8 - CAPEX and OPEX of the various technologies considered in this study[55]

	CAPEX	OPEX	Period
PEM electrolyser	0.540 M€$_{2015}$/MW	3.2% of CAPEX/year	50000 hours
Solar PV	0.380 M€$_{2015}$/MW	2.3% of CAPEX/year	25 years
Wind	1.000 M€$_{2015}$/MW	1.2% of CAPEX/year	25 years~
RO desalination	0.45 M€$_{2015}$	2% of CAPEX/year	20 years
MSFD desalination	0.45 M€$_{2015}$	2% of CAPEX/year	20 years

The table 9 shows the variable costs related to water:

Table 9 - Variable costs

	Variable costs (€)
Electricity price	30,79 €/MWh
Access tariff for injection in transmission network	0,49 €/MWh
Average tariff on access to electricity network	22,70 €/MWh
Water (drinking quality)	1.89 €/m^3
Water grid access tariff	19777 €/year
Storage tank construction	200 €/m^3

The annualized CAPEX is calculated by the expression (26):

$$a = \frac{Ci}{1 - (1+i)^{-lifetime}} \quad (26)$$

Where,

a – Annualized investment cost;

C – Total investment cost of technology (CAPEX);

i – Rate charged on the loan;

lifetime – Lifespan of equipment;

The Levelized Cost Of Water (LCOW) of the desalination plant is calculated by the expression (27):

$$LCOW = \frac{CAPEX \times CRF + OPEX + EC}{TWP} \qquad (27)$$

Where,

LCOW – Levelized Cost Of Water;

CAPEX – Capital expenditure;

CRF – Capital Recovery Method/Annualized investment cost;

OPEX – Operating expenditure;

EC – Energy Costs;

TWP – Total annual desalinated water;

Such expressions allow the calculation of the necessary parameters of each combination according to its operation mode. The parameters that will be obtained for this economical analysis are the following:

- Total annualized costs of the desalination unit;
- Levelized cost of water (LCOW);
- Electricity costs;

4. Results

The technical and economical results are set to be analyzed and discussed. The technical results will show the viability of the desalination and storage unit of each scenario and combination. The economical results will estimate the associated costs of building the desalination and storage unit, which differ for each scenario and combination.

4.1. Technical analysis

Each operating mode has a different specification. Mode B was designed to understand the electrolyzer operation when using only one RES and without energy consumption from the national grid. Mode C was designed in order to simulate the operation of the electrolyzer using a hybrid renewable production system. Lastly, mode E was designed to understand the performance of the electrolyzer working at a minimum load of

20% of nominal capacity using a combination of RES. This configuration is expected to consume energy from the grid when renewable power falls below 20% of electrolyzer nominal capacity.

EnergyPLAN allows calculating the total annual H_2 production as well as the production in each hour of the year. From the analysis of this hourly profile it is possible to extract the maximum hourly production during the year. Table 10 shows the estimates of hydrogen production of each combination, in kt:

Table 10: Estimates of annual of hydrogen production and maximum production of each combination[50]

Combination	Annual hydrogen production (kt/a)	Maximum hourly production (kt/h)
Bs2E3P	116.899	0.056
Cs1E2P1W	93.217	0.033
Cw1E2P1W	96.366	0.033
Ew1E2P1W	95.992	0.033

The performance of the desalination unit is analyzed, according to each combination and taking into consideration the fact that the water dissociation efficiency of the electrolyzer is 50%, as explained above. The corresponding amounts of water, in m^3, are shown in Table 11:

Table 11: Estimates of annual water consumption and maximum hourly water consumption of each combination

Combination	Annual water consumption (m^3/a)	Maximum hourly water consumption (m^3/h)
Bs2E3P	$10.5\text{x}10^5$	510.48
Cs1E2P1W	$8.3\text{x}10^5$	298.35
Cw1E2P1W	$8.6\text{x}10^5$	305.32
Ew1E2P1W	$8.6\text{x}10^5$	300.00

The values shown in Table 11 also define the total capacity of the desalination unit. The total capacity can be defined from the maximum hourly values of water consumption for each combination, which is obtained by multiplying the maximum hourly water consumption value by 24 hours and 366 days. Figure 20 shows the annual water requirements of each combination, compared to the annual water consumption of the Sines municipality in 2019[56]. The Sines coal plant used large amounts of industrial water annually, averaging $2.3\text{x}10^6$ m^3.

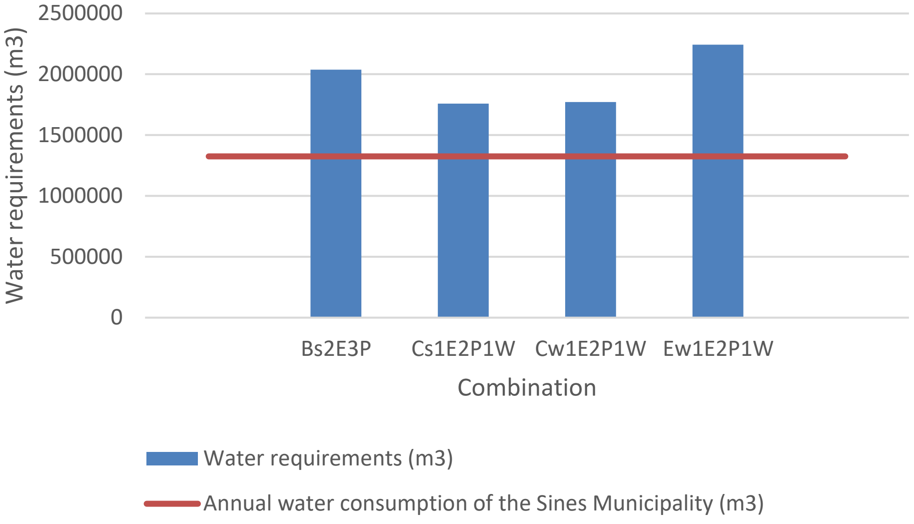

Figure 20 – Water requirements of each combination in comparison to the annual water consumption of the Sines municipality, in m^3

Having the water requirements of each combination, two different operation modes of the desalination unit were established. The first operation mode defined to be a continuous operation mode of the desalination unit, where the water supply needs of the electrolyzer are instantaneously supplied by the desalination unit, using energy either from the RES or the national grid. For the second operation mode we start by considering the electricity consumption of the electrolyzer plant without the desalination unit. We then impose the constraint that the same amount of electricity will have to be used to feed both the electrolyzer and the desalination unit, implying a reduction in hydrogen production.

The first operation mode is relatively simple as it consists of using part of the excess energy produced by the RES. This operation mode is only problematic if there is no excess energy production from the RES.

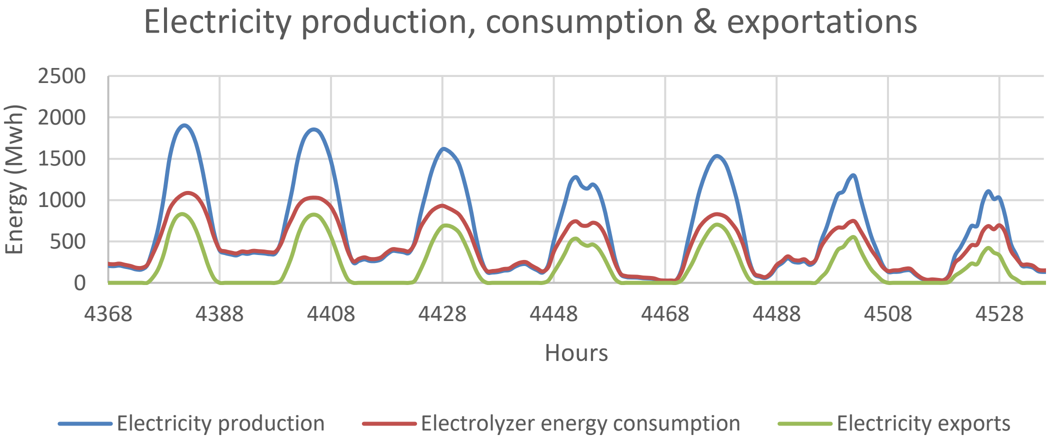

Figure 21 – Electricity production, consumption and exports of CW_1E_2P_1W

It is important to verify if the excess electricity production (exports) can supply electricity to the desalination unit. While the annual electricity exportation may appear to be enough to supply the desalination unit, there are periods where there are no electricity exports, as Figure 21 shows. This occurs in periods of low production, generally at night, where there is no electricity generated from solar photovoltaic. As such, in those moments the electrolyzer will use the energy in its entirety to produce hydrogen, and there will be no electricity from the RES for desalination.

In such cases, the desalination unit is expected to withdraw the necessary energy from the grid.

To understand the energy demands of the desalination unit, the electricity consumption of the desalination plant for each combination was calculated. This value can be obtained by considering the hourly water demand and the efficiency of the desalination plant, which is set to be an average of 5 kwh/m^3, as Table 5 shows. Table 12 shows the annual electricity consumption of the desalination plant for each combination in comparison to the annual electricity consumption of the electrolyzer, in Gwh/year:

Table 12: Electricity consumption of the desalination plant for each combination in comparison to the electricity consumption of the electrolyzer, in Gwh/year

Combination	**Electricity consumption of desalination plant, Gwh/year**	**Electricity consumption of electrolyzer, Gwh/year**
Bs2E3P	10.190	5337.862
Cs1E2P1W	8.800	4256.501
Cw1E2P1W	8.866	4400.277
Ew1E2P1W	11.217	4383.206

Because of the low desalination unit electricity consumption, there is a relatively large difference of energy consumption when compared to the electricity that the electrolyzer requires. Therefore, the energy requirements for the desalination are substantially lower than the electrolyzer, over 1000 times lower in some cases. Figures 22 to 25 shows the hourly values of the electricity exports and the electricity consumption of the desalination unit in a week of the four combinations:

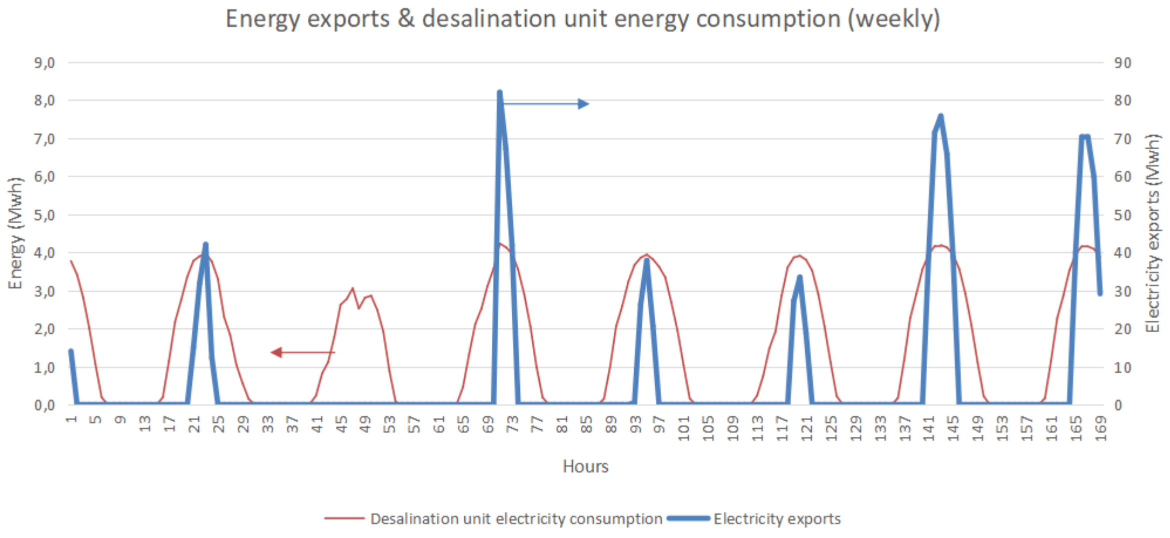

Figure 22 – Electricity exports and electricity consumption of the desalination unit throughout a week, of the combination BS_2E_3P

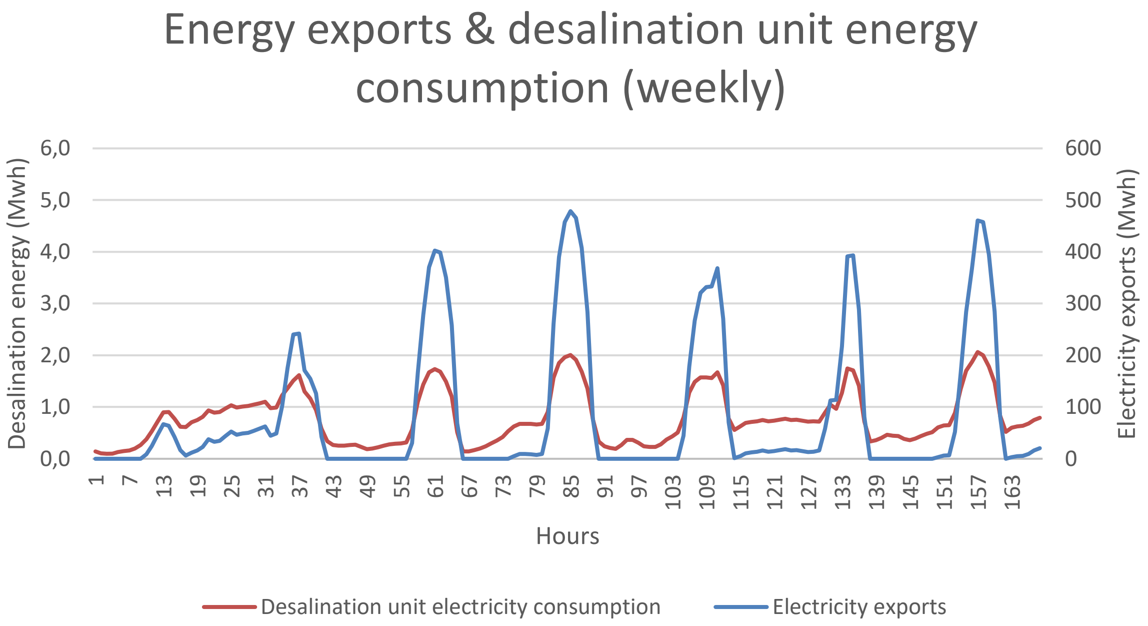

Figure 23 – Electricity exports and electricity consumption of the desalination unit throughout a week, of the combination CS_1E_2P_1W

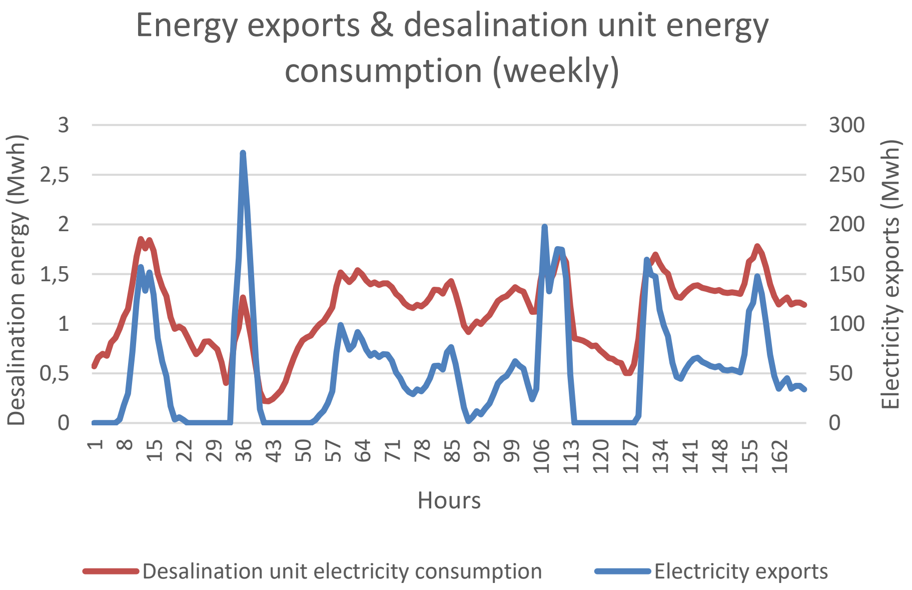

Figure 24 – Electricity exports and electricity consumption of the desalination unit throughout a week, of the combination CW_1E_2P_1W

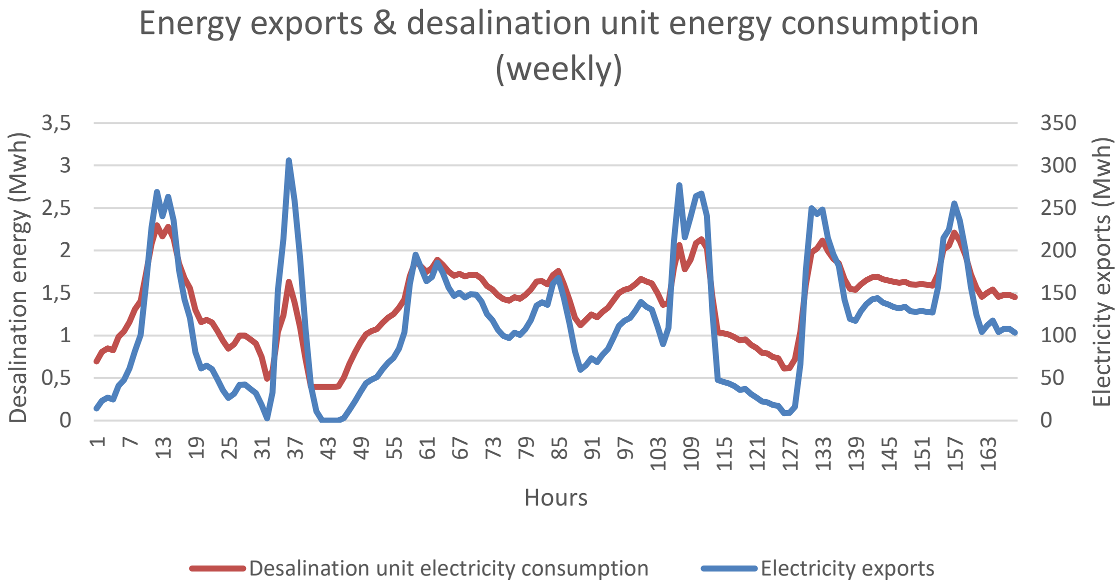

Figure 25 – Electricity exports and electricity consumption of the desalination unit throughout a week, of the combination EW_1E_2P_1W

The lack of energy for desalination in certain periods has made it necessary to calculate how much electricity the desalination unit will withdraw from the national grid. This was done by calculating the total electricity the desalination unit uses in periods where the energy exports are 0, which are during the darker hours, that usually account for 9 hours in one day. Table 13 shows the electricity the desalination unit uses from the grid.

Table 13: Electricity consumption of the desalination plant, the amount of electricity used from the grid and its percentage for each combination, in Gwh/year

Combination	Electricity consumption of desalination plant, Gwh/year	Electricity consumption from grid, Gwh/year	% from grid
Bs2E3P	10.190	5.582	54.779
Cs1E2P1W	8.800	0.760	8.636
Cw1E2P1W	8.866	1.560	17.595
Ew1E2P1W	11.217	0.800	7.132

The second operation mode is set to work at a reduced hydrogen production to avoid energy consumption from the energy grid by the desalination unit.

In this mode, the total electricity consumed by the electrolyzer is now shared between the electrolyzer and desalination unit and consequently, the hydrogen production is reduced. The reduced hydrogen production was calculated by using the following equation (28):

$$Energy\ H_2(2) = Energy\ H_2(1) \times \left(\frac{Energy\ H_2(1)}{Total\ (1)}\right) \qquad (28)$$

Where,

Energy $H_2(2)$ – Energy used by the electrolyzer in the second operation mode

Energy $H_2(1)$ – Energy used by the electrolyzer in the first operation mode

Total(1) – Sum of energy used by the electrolyzer and desalination unit in the first operation mode

This equation allows the calculation of the energy that the electrolyzer uses in the second operation mode. A similar equation (29) can be used for calculating the energy which the desalination unit uses:

$$Energy\ H_2O(2) = Energy\ H_2(1) \times (\frac{Energy\ H_2O(1)}{Total\ (1)}) \quad (29)$$

Where,

Energy $H_2(2)$ – Energy used by the electrolyzer in the second operation mode

Energy $H_2O(2)$ – Energy used by the desalination unit in the second operation mode

Energy $H_2O(1)$ – Energy used by the desalination unit in the first operation mode

Total(1) – Sum of energy used by the electrolyzer and desalination unit in the first operation mode

These equations are used to obtain an approximation of the energy spent in the second operation mode. Although the hydrogen production is changed, the values are not significantly reduced, because of the low energy requirements of the desalination unit. Table 14 shows the estimates of reduced hydrogen production of each combination, in kt:

Table 14: Estimates of reduced hydrogen production of each combination, in kt

Combination	Hydrogen production of first operation mode (kt/a)	Hydrogen production of second operation mode (kt/a)	Reduction in hydrogen production (%)
Bs2E3P	116.899	116.787	-0.095
Cs1E2P1W	93.217	93.121	-0.102
Cw1E2P1W	96.366	96.269	-0.100
Ew1E2P1W	95.992	95.869	-0.128

As expected, the hydrogen production only is slightly lower. The differences account for around less 100kg of hydrogen produced on a year. A reduced hydrogen production also lowers the water requirements for the desalination unit since less water is used for the electrolysis process. The water requirements of the desalination unit are calculated directly from the hourly energy consumption profile of the electrolyzer. Table 15 shows the water requirements of the desalination unit for each combination, in m^3:

Table 15: Water requirements of the desalination unit for each combination, in m^3:

Combination	Water requirements for first operation mode (m^3)	Water requirements for second operation mode (m^3)
Bs2E3P	2.104 $x10^6$	2.102 $x10^6$
Cs1E2P1W	1.677 $x10^6$	1.676 $x10^6$
Cw1E2P1W	1.734 $x10^6$	1.732 $x10^6$
Ew1E2P1W	1.727 $x10^6$	1.725 $x10^6$

Considering this reduction, the electricity consumption of the electrolyzer was estimated from equation (29). Table 16 shows the corrected values of the electricity consumption of the desalination unit and the electrolyzer:

Table 16: Electricity consumption of the desalination plant for each combination in comparison to the electricity consumption of the electrolyzer, in Gwh/year

Combination	Electricity consumption of desalination plant (Gwh/year)	Electricity consumption of electrolyzer (Gwh/year)
Bs2E3P	10.170	5332.771
Cs1E2P1W	8.781	4252.106
Cw1E2P1W	8.848	4395.847
Ew1E2P1W	11.188	4367.604

4.2. Economic analysis

Certain parameters were calculated for the economic analysis, namely the annualized investment costs and LCOW (equations 26 and 27). To obtain such values, it is necessary to know the price of the desalination unit. Since the capacity of the desalination unit of the combinations ranges 1000-10000 m^3/day, it is considered a medium sized desalination unit[57]. Generally, the water desalination costs vary, depending on several factors, namely the capacity of the desalination plant, the technology that is used and the energy source. For example, the water costs of a high-capacity MSF desalination plant (23000 – 528000 m^3/day) ranges 0.51 – 1.61 €/m^3 while a RO desalination plant of the same capacity ranges 0.41 – 0.61 €/m^3 [58]. In some cases, renewable desalination is calculated to cost as high as 2.66 €/m^3, however considering that the renewable energy costs are decreasing, these estimations are set to decrease[59]. Table 17 shows some of the costs of desalination technologies according to the capacity[57]:

Table 17: Average water production cost according to the technology and capacity[57]

Technology and capacity	Cost of water (€/m^3)
MSF 23000 – 528000 m^3/day	0.51 – 1.61
RO 100000 – 320000 m^3/day 15000 – 60000 m^3/day 1000 – 4800 m^3/day	0.41 – 0.61 0.44 – 1.49 0.64 – 1.52

The CAPEX value of each combination was calculated by taking into account the desalination price for the size of the desalination unit (a value of 1.72 €/m^3 was assumed, taking into consideration the price range of medium sized RO plants of 0.262-1.72 €/m^3)[57], the construction cost[60] and the desalination plant capacity. This value is necessary for further calculations. The construction costs were estimated from the capital cost of other desalination plants in one study[61], assuming a direct proportion relation in plant size x capital cost between their specifications and ours (i.e., a desalination plant of 365000 m^3/a capacity was estimated to cost 350000 €, therefore a desalination plant of 9000000 m^3/a capacity will have a construction price set at around 8600000 €). The OPEX values are assumed to be 2% of the CAPEX. Table 18 shows the capacity and CAPEX for desalination of each combination, considering a desalination plant cost of 1.72 €/m^3:

Table 18: Desalination plant capacity, CAPEX and construction costs values for each combination

Combination	Capacity (m^3/a)	CAPEX (€)	Construction costs (€)
Bs2E3P	8968112.64	15425154	8638872
Cs1E2P1W	5241412.80	9015230	5026012
Cw1E2P1W	5363861.76	9225842	5143429
Ew1E2P1W	5270400.00	9065088	5053808

The CRF of the combinations was calculated by assuming an interest rate of 3% for the desalination unit over the course of 20 years, which is 0.067. This value is necessary for calculating the LCOW.

The annualized investment cost was calculated for each combination using equation [26]. The values are different from each combination due to the CAPEX values. Table 19 shows the annualized investment costs of each combination:

Table 19: Annualized investment costs of each combination, in €

Combination	Annualized investment costs (€)
Bs2E3P	1036813
Cs1E2P1W	605965
Cw1E2P1W	620122
Ew1E2P1W	609316

Unlike the CAPEX and annualized values, the LCOW value of each combination varies depending on the operation mode. As equation (27) shows, the LCOW expression considers the values of CAPEX, CRF, OPEX and energy costs. This means that the LCOW of the first operation mode will be higher than the LCOW of the second operation mode, since the second operation mode has no energy costs for desalination.

The energy costs of each combination of the first operation mode were calculated by multiplying the electricity that the combination uses (Table 11) by the electricity price and tariff access price (Table 8). These values are considered variable costs. The energy costs of the second operation mode are zero.

The LCOW cost was calculated for the first and second operation mode using equation (27). Figure 26 shows the LCOW values for each combination of the first operation mode, in €/m^3:

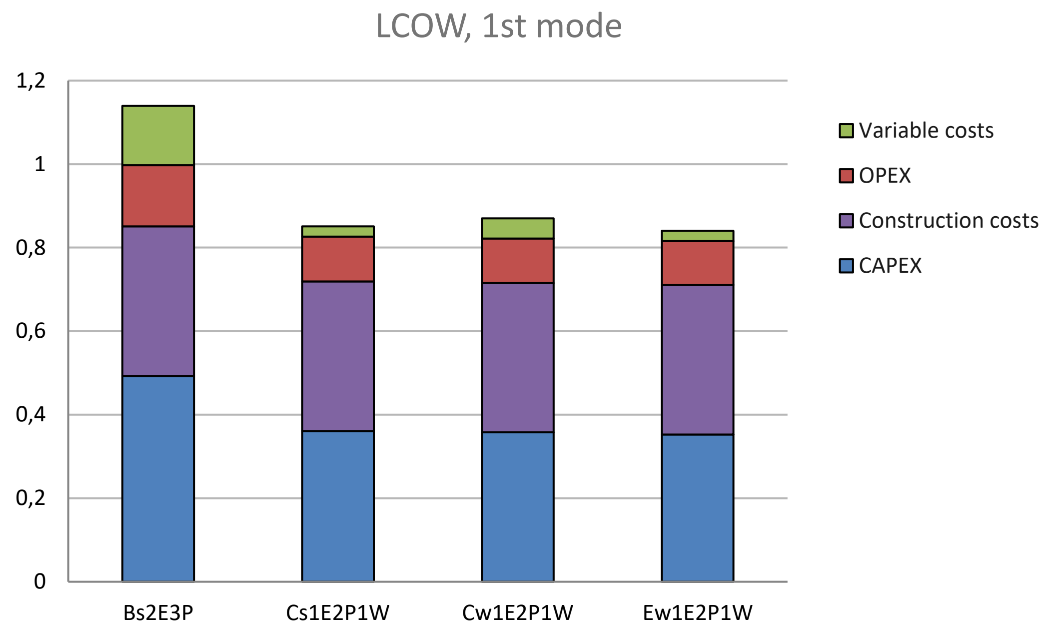

Figure 26 – LCOW values of each combination of the first operation mode, in €/m^3

Figure 27 shows the LCOW values for each combination of the second operation mode, in €/m^3:

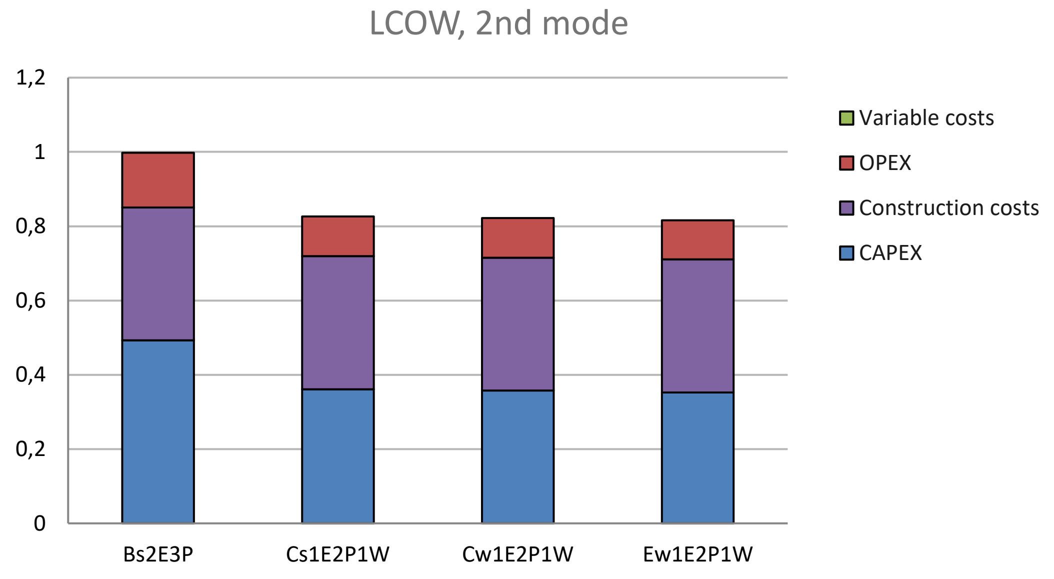

Figure 27 – LCOW values of each combination of the second operation mode, in €/m^3

The maximum LCOW value is roughly 1.14 €/m^3, which belongs to Bs_2E_3P on the first operation mode. The remaining LCOW values are mostly close to 0.85 €/m^3 on either operation modes.

The LCOW values obtained for the two operation modes are significantly lower than the value of 2.0571 €/m^3 charged for potable water by the local water utility (Águas de Santo André) to industrial customers that consume more than 150 m^3 per month[62]. The value charged for industrial water is 0.4223 €/m^3. So the cost of desalinated water is within the range of utility water prices. Furthermore, desalination would make use of a much more abundant resource (sea water) than the fresh water supplies in the region. This is an expected result, as the desalination unit benefits from the energy produced by the RES, decreasing costs.

It is important to understand the economic impact the desalination plant has; namely how much it changes the LCOH (Levelized Cost Of Hydrogen). The LCOH value is obtained by dividing the total annual costs of the plant by the quantity of hydrogen produced[62]. While the hydrogen production stays the same, only changing slightly on the second operation mode, the total annual costs increase with the addition of a desalination plant.

Table 20 shows the LCOH value before the addition of the desalination plant, the calculated annual costs and the adjusted LCOH value:

Table 20: LCOH values and annual costs

Combination	**Annual cost (M€)**[63]	**LCOH (€/kg)**[62]	**Adjusted annual cost (M€)**	**Adjusted LCOH (€/kg)**	**% increase in LCOH**
BS_2E_3P	174.03	1.487	175.066	1.497	0.672
CS_1E_2P_1W	152.29	1.637	152.895	1.644	0.428
Cw_1E_2P_1W	155.78	1.675	156.400	1.681	0.358
EW_1E_2P_1W	162.86	1.679	163.469	1.702	1.370

The LCOH value does not change significantly, due to the low annual cost of the desalination plant. The LCOW and LCOH values differ since the LCOH includes the investment costs of the RES.

5. Conclusions and further work

The study widened the scope of a previous work that concentrated on the technical and economic analysis of a GW-scale electrolysis facility. That study analyzed 144 different configurations with different weather conditions and technical specifications. Of those configurations, we chose the 4 that consistently presented optimum techno-economic performance (for different values of discount rate) and analyzed the impact of the introduction of a desalination plant to the system.

The annual amount of water necessary to feed the electrolyzers in any of the four cases considered is always significantly higher than the annual domestic water consumption in the Sines municipality (14304 inhabitants in 2021). It is therefore evident that desalination would avoid a significant burden on existing water supply.

The desalination plant that we analyzed in this work has a capacity in the range 5.24-8.97 Mm^3/year, that qualifies as medium size plant. We have considered that the desalination plant should be capable of satisfying the instantaneous needs of the electrolyzer. As such, the water production profile of the desalination unit is directly obtained from the amount of H_2 the electrolyzer produces, which vary depending on the RES combination that provides electricity to the system.

Because the RES used to power the hydrogen production plant provide significant excesses of electricity production, we have studied operation modes of the desalinator that can make the best use of this excess electricity. Two operation modes were designed.

The first operation mode uses excess RES electricity to power the desalination unit. In the periods when such excess electricity production is not available the desalination unit would withdraw energy from the grid.

The second operation mode was created to address that problem and considers a reduced H_2 production profile to ensure no withdrawals from the energy grid. As such, the H_2 production, water production and energy requirements for the processes are slightly reduced. These adjustments would be quite insignificant for the overall process. For example, the reduction of H_2 production would reflect only a quantity of less 100 tons of H_2 produced in one year, which accounts for a reduction of about 0.1% of the total quantity of H_2.

It was concluded that regardless of the operation mode, the desalination unit has a very low energy consumption profile, especially when compared to the electrolyzer, as the energy consumption of the desalination unit is about 500 times lower than the electrolyzer for all the configurations.

One important contribution for the viability of such desalination plant is the fact that it uses energy, partially or in its entirety, from the renewable energy park that is modelled for the electrolyzer of each configuration. While a desalination plant of such dimensions would not require a large-scale renewable energy park such construction, even if small-scale, would make the project less sustainable.

In terms of the economic analysis certain figures were estimated which can give an overall idea on the project costs.

The levelized cost of water (LCOW) values were obtained by dividing the total annualized cost by the total annual production of water. The total annualized costs were estimated from the CAPEX, OPEX, and variable costs. For the first operation mode, the LCOW is in the range of 0.840-1.140 €/m^3. The first operation mode has to consider variable costs which consist of energy withdrawals from the grid, which increases costs.

For the second operation mode, the LCOW is in the range of 0.816-0.998 €/m^3. The LCOW of the second operation mode is generally lower than the LCOW of the first operation mode because in the present case there is no use of grid electricity and therefore the variable costs are lower.

The LCOW values obtained for the two operation modes are significantly lower than the value of 2.0571 €/m^3 charged for potable water by the local water utility to industrial customers that consume more than 150 m^3 per month. The value charged for industrial water is 0.4223 €/m^3. So, the cost of desalinated water is within the range of utility water prices. Furthermore, desalination would make use of a much more abundant resource (seawater) than the freshwater supplies in the region.

The other factor to take into account is how the desalination unit would add to the cost of production of hydrogen. Since the LCOH is calculated from the annualized costs, the adjusted LCOH is obtained by including the desalination annualized costs to the H_2 production plant annual costs. Overall, the installation of the desalinator increases the LCOH by less than 1%.

The study has demonstrated that the addition of a desalination unit to the H_2 production plant would be viable.

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