



Leveraging the competitive advantages of end-of-life underground coal mines to maximise the creation of green and quality jobs

Grant Agreement 101057789

## **Deliverable 2.6**

**“Green Hydrogen Deployment”**

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## Executive Summary

The present document constitutes the Deliverable 2.6 “Green Hydrogen deployment” in the framework of the project titled “Leveraging the competitive advantages of end-of-life underground coal mines to maximise the creation of green and quality jobs” (Project Acronym: GreenJOBS, Grant Agreement No 101057789).

This document has been prepared to provide a detailed description of the activities within Task 2.3 (T2.3), entitled “A new energetic vector: Green hydrogen”, on the scope of Work Package 2 (WP2), entitled “Deploying circular economy technologies”.

A description about Hydrogen technology is included as a rapidly evolving field that focuses on the production, storage, and utilization of hydrogen as a clean and sustainable energy carrier. Hydrogen has the potential to play a pivotal role in decarbonizing energy systems, powering transportation with zero-emissions, generating electricity in fuel cells, and replacing fossil fuels in industrial processes.

The implementation of this hydrogen technology in mining areas holds promising potential for addressing key challenges. One feature of hydrogen technology in mining is its ability to provide clean and green energy joined to solar or wind sources. This presents significant opportunities for economic growth, job creation, and environmental sustainability, making it a promising solution for addressing global energy and climate challenges.

There is some pioneering initiative focused on repurposing end-of-life coal mines to generate renewable hydrogen. The MINE-TO-H<sub>2</sub> project, promoted by the Consortium formed by HUNOSA, DURO FELGUERA, NORTEGAS, UNIOVI and GIG, is taken as a reference of application of these processes in this type of areas.

Finally, at the end of this document, an evaluation of a project in economic terms is considered.

## 1 Introduction

This report focuses on the overarching topic of "Green Hydrogen Deployment". This is part of the work package N° 2 for further processing of the funded EU project GreenJOBS under the consortium leadership of the Universidad de Oviedo (UNIOVI).

Currently, the mining regions that have been carrying out this activity for many years, are in the process of transition towards new models of development and activities. This need for research links in a good way with the development and progress of the implementation of renewable energy sources and the decarbonisation technologies where they can take advantage of their strengths, facilities, industrial fabric and knowledge for their implementation.

Hydrogen has the potential to provide safe, economically competitive, environmental friendly and emission-free energy, but its current penetration in the energy sector is still limited. Hydrogen has the potential to replace fossil fuels in the main areas of energy consumption, including, industrial, transport and, even, buildings sectors, making it a competitive and complementary solution to electrification to achieve a future without emissions. It can cover the energy needs of these sectors even when they are large, require seasonal storage or do not admit electrification.

Hydrogen can compensate for the intermittency of renewable energies by acting as a transportable energy carrier and storable in the gas infrastructures that already exist in most developed countries. Therefore, it is important to assess the storage capacity of the existing gas transmission network and the modifications needed to accommodate to hydrogen or to hydrogen combined with natural gas. Therefore low-carbon hydrogen is a part of the different national plans that form the EU hydrogen strategy and in line with the European Green Deal as the most important document for the decarbonisation of the EU economy by 2050.

The electrification of the economy and decarbonisation of the electricity sector are the primary goals of the European Green Deal, but in the activities where the electrification is not competitive the use of renewable hydrogen can play a crucial role for decarbonising these sectors with hard-to-abate emissions.

Therefore, the EU presented a strategy for the development of the hydrogen market in Europe to produce 10 million Mg of zero emissions H<sub>2</sub> and instal 40 GW by 2030. The REpowerEU Plan reenforces this objective of the Strategy with an additional supply of 10 millions Mg of zero emissions Hydrogen by 2030.

Green hydrogen, produced by the electrolysis of water from a coal mine (after right treatment) and electricity from renewable sources, a clear alternative generating zero emissions hydrogen and contributing, in this way, to supply the emerging hydrogen demand in Europe. Again, technical specifications, cost data, and operational constraints will be analysed.

A detailed assessment of job creation potential per MW installed or per MW of electrolyzers capacity installed for commissioning and operation will be developed. The urge to reduce greenhouse gas emissions, the increasing costs for CO<sub>2</sub> emission certificates, and the increasing ambition in climate mitigation put pressure on conventional production processes in energy-intensive industries such as steel, cement, chemicals, and others.

Green hydrogen becomes an interesting option to increase decarbonisation as other solution and this can be useful in operational proceses. According to the definition green hydrogen as coming from water electrolysis that's powered by newly built renewable electricity generation equipment. Green hydrogen can also play a complementary role to help the renewable electricity implementation as an energy storage system (even seasonal) thanks to its large volume and extended lifetime in a similar way to how strategic reserves of natural gas or oil is used, making it possible supplying renewable hydrogen reserves to support the electricity grid.

FAEN will lead this task with the cooperation of UNIOVI, GIG and DMT-THGA.

## 2 Hydrogen Technology

Renewable hydrogen will be a crucial technology in achieving the European ambitious goal to become the first climate neutral continent for 2050, but its successful implementation requires appropriate regulation and a drive to develop knowledge and technology for its production, storage, transport and use.

To promote the successful deployment of hydrogen, there are several reinforcing reasons, including, among others, the higher efficiency than combustion engines, the longer durability of fuel cells, scalability of hydrogen technology from small portable devices to large power plants, versatility as fuel for a wide range of energy needs as transportation, heating and power generation.

Technological advancements have led to lower production costs and increased use of hydrogen, but scaling up technologies for effective commercialisation and defining a roadmap for optimising the investment plan required for hydrogen deployment remains essential.

Significant technological advancements have been made in the entire hydrogen value chain over the last decade, resulting in falling renewable production costs, making renewable hydrogen production cost-competitive with non-renewable processes in certain locations in the medium term. Therefore, renewable hydrogen can play a crucial role in achieving a clean energy future and effective decarbonization of the economy. Social demands and technological advancements go hand in hand to promote the role of hydrogen as a real alternative to reduce CO<sub>2</sub> emissions, and renewable hydrogen's penetration in our society is crucial to achieving climate objectives.

### 2.1 Hydrogen properties

Hydrogen is the most abundant element in the universe and consists of a single proton and a single electron, making it the simplest and smallest chemical element. Although it is widely present in stars and gaseous planets, it is not usually naturally pure on Earth, and thus requires industrial methods for production. Hydrogen is created by combining two atoms of the element, resulting in a gas that is odorless, colorless, and tasteless. It is not very soluble in water or other solvents, but it does dissolve well in certain metals, including iron, nickel, platinum, and palladium.



Table 2-1 shows the values for the mean parameters and physical and chemical characteristics for hydrogen.

Table 2-1. Hydrogen properties

PARAMETER	VALUE
Density of hydrogen gas	0,0899 kg/Nm <sup>3</sup>
Density of liquid hydrogen	0,0708 kg/L
Energy density of hydrogen gas	10,8 MJ/Nm <sup>3</sup>
Energy density of liquid hydrogen	8,495 MJ/L
Boiling point	20,28 K
Melting point	14,02 K
Lower Calorific Value	119,972 MJ/kg
Upper Calorific Value	141,890 MJ/kg
Explosion limits	4-75 % del H <sub>2</sub> in air
Detonation limits	18,3 – 59,0 % of H <sub>2</sub> in air
Spontaneous combustion temperatures	858 K
Specific heat capacity (P cte)	C <sub>p</sub> = 14,33 J/(kgK)
Specific heat capacity (V cte)	C <sub>v</sub> = 10,12 J/(kgK)
Diffusion coefficient	0,61 cm <sup>2</sup> /s

### 2.1.1 Hydrogen as energy carrier

The hydrogen economy encompasses various technologies related to the production, storage, distribution, and utilization of hydrogen and its derivatives across different sectors of the economy.

Hydrogen can be produced using a variety of methods, including electrolysis, reforming of fossil fuels, and biomass gasification. Once produced, hydrogen can be stored in various forms such as compressed gas, liquid, or solid-state storage. The distribution of

hydrogen involves transporting it through pipelines, trucks, or other means to the end-users.

In terms of utilization, hydrogen can be used as a raw material in some industries, like fertilizers, reductor agent in some process, like the reduction of iron ore in the Steel industry, as a fuel in industrial furnaces and boilers or in the transportation, including fuel cell vehicles and hydrogen-powered trains. Moreover, hydrogen can be combined with other gases to produce syngas, which can be further processed into various fuels and chemicals.

Overall, the development of the hydrogen economy requires significant investments in research and development, infrastructure, and policy support to achieve widespread adoption and integration with existing energy systems.

Hydrogen is being considered as a new and environment friendly energy Carrier. It seems to be a potential alternative to traditional energy carriers based on fossil fuels. Although there are some natural deposits of hydrogen, most of the hydrogen consumed is obtained by other sources. Nowadays it is but rather an energy carrier that can be produced from traditional energy systems such as natural gas. In order to view hydrogen as a clean fuel that can be produced on a large scale, it is important to explore renewable energy sources that can generate this gas.

The production of hydrogen from renewable energy sources can allow for distributed generation, which aligns with local economies and utilises the cleanest and most suitable methods for each region. It also has the potential to reduce the reliance on imported fossil fuels, as hydrogen can be produced locally in many cases. Thus, the adoption of hydrogen as an energy carrier can contribute to the sustainable development of society by reducing pollutants and ensuring a reliable energy supply at affordable prices.

To produce hydrogen on a large scale in the future, experts agree that solar energy production or nuclear energy (in countries that use it) will be necessary. In the short to medium term, the best way to enable the penetration of renewable hydrogen will be through production from wind or solar photovoltaic energy, or by biofuel reforming. This is mainly due to the decentralised nature of these production methods, which increases their competitiveness.

Excess renewable energy can be utilised by converting it into hydrogen and using it in a variety of ways.

One option is to transform excess renewable energy into hydrogen, store it, and transform it back into hydrogen using a fuel cell, internal combustion engine, or microturbine. This allows renewable energy parks to be made manageable, increasing their competitiveness.

Another option is to transform excess renewable energy into hydrogen, store it, and distribute it to hydrogen plants or refuelling points, where it can be consumed as fuel by fuel cell electric vehicles or internal combustion vehicles modified to run on hydrogen. This reduces imports of fossil fuels and greenhouse gas emissions.

Excess renewable energy can also be transformed into hydrogen and injected into the natural gas grid, allowing it to be stored due to the large capacity of the natural gas grids.

Renewable ammonia can be generated by zero emissions hydrogen with nitrogen, which can be used in the fertilizer industry, explosives, or as an energy carrier. Renewable ethanol and/or methanol can also be generated by blending hydrogen from excess renewable energy with CO<sub>2</sub>, which can be used in the chemical and ancillary industries or as an energy carrier.

Each of these methods has different technical and economic conditions, so it is necessary to study the energy and energy balances of each process and use the one that maximises the benefits depending on the existing conditions. Remote management can also be used to integrate multiple renewable energy installations with their corresponding excesses, reducing the overall cost of the installations.

Creating incentives to build supply and demand is crucial, including bridging the cost gap between conventional solutions and renewable and low-carbon hydrogen solutions, and by establishing appropriate state aid rules and providing funding for hydrogen technologies.



## 2.2 Hydrogen in transition

Hydrogen is a versatile and safe fuel that has been used for decades in the chemical and petrochemical industry as well as in other industrial applications. Currently, more than 70 million Mg of hydrogen are produced worldwide, of which more than 90% are for industrial use. This hydrogen is produced mainly in the conventional way –produced by various processes that use fossil fuels. These processes are primarily steam reforming of natural gas, coal gasification or separation from coke oven gas. It accounts for as much as 76% of the hydrogen produced in the world.

Hydrogen is also a commodity that serves as a fuel for fuel cells, engines, and gas turbines. It can be transported and stored as compressed hydrogen or in combination with other molecules such as ammonia or methanol.

The production, transport, storage, and uses of hydrogen continue to develop in anticipation of its use in new areas that will give rise to large markets driven by new regulations to address climate change and the energy transition. This includes the mobility sector, the industrial sector the storage of renewable electrical energy in fuels or Power-to-X.

The transformation of excess of renewable energy into hydrogen has been mentioned above.

When it comes to transport based on electric mobility, the use of hydrogen can be argued against the direct use of electricity from batteries. The enormous needs of transport can be grouped into three major groups, with blurred lines of separation, but which allow us to foresee where hydrogen will play an essential role: battery electric vehicles (BEVs), hydrogen fuel cell electric vehicles (FCVs), and vehicles based on bio- or synthesized liquid fuels (some of them using Hydrogen as a raw material).

BEVs are the recommended solution for vehicles weighing only a few Mg and with a daily mileage range of less than 100 kilometers, which corresponds to urban mobility with small vehicles. However, as the daily mileage or the weight of the vehicles increases, such as buses or cargo trucks, this solution becomes less suitable.

FCVs are the solution for covering greater distance ranges and transporting heavier weights, such as long buses, intercity buses, cargo trucks, refuse collection trucks, trucks used in mining, construction, goods delivery, cranes, trains, and even river and maritime transport.

Hydrogen, therefore, represents a pathway for the energy transition from fossil fuels to renewable sources in the transport. Its use could largely replace the current uses of natural gas and open up enormous market expansion prospects in heavy land transport, rail, river, light maritime transport, and even light air transport.

In the field of industry there are many processes from various sectors that emit greenhouse gases difficult to abate. In such cases, hydrogen is presented as an interesting and promising alternative for the substitution of fossil fuels for clean and renewable energy. The main processes for their volume and importance are:

Reducing emissions in steel production: Hydrogen can be used as an agent to reduce iron and produce steel without emitting carbon dioxide. This is known as hydrogen steel production, and is expected to be a key technology for reducing emissions in the steel industry.

Chemical processes: hydrogen is used in a variety of chemical processes. The most important is the production of ammonia, which is used as fertilizer. It can also be used in the production of many chemicals such as methanol and propylene. In refinery, Hydrogen is used in different processes, among which hydrotreatment is one of the most important, in order to eliminate products harmful to the environment. The process consists of the addition of hydrogen to induce hydrogenation and hydrogenolysis reactions.

Other reactions where hydrogen is a raw material in refinery processes are Hydrodesulphurisation (in which sulfur-containing compounds are removed to produce hydrogen sulfide or hydrogen sulfide), Hydroisomerization (where paraffins are converted to isoparaffins), Disallocation (where aromatic compounds are hydrogenated to cyclaraphines or alkanes), Hydrocracking (where long-chain hydrocarbons break down to form shorter chains in the gasoline range).

In recent decades, the demand for hydrogen for refineries has been increasing due to increased consumption of refining products.

In conclusion, hydrogen is a safe and versatile fuel that has been used for decades in various industries. Its use in new areas such as the mobility sector, in the energy intensive industries and in the storage of renewable electrical energy in fuels or Power-to-X could lead to significant market expansion. Hydrogen represents a pathway for the energy transition from fossil fuels to renewable sources, and its use could help reduce greenhouse gas emissions and improve air quality. The different potential sources of hydrogen generation and their associated processes have been described but to consider hydrogen as a decarbonization vector it is necessary to ensure that it is an emission-free hydrogen. To distinguish the types of hydrogen, it is classified in colors based on its environmental impact during its production.

### 2.2.1 From grey to green hydrogen

To distinguish the different process of production the hydrogen is classified in colors based on its environmental impact. This classification is simple, but allows easy identification of the type of hydrogen. In addition, the definition of each typology is perfectly established and quantified.



White Hydrogen

Gray/Brown/Black Hydrogen

Blue Hydrogen

Orange/Amber Hydrogen

**Green Hydrogen**

Pink Hydrogen

Turquoise Hydrogen

#### 2.2.1.1 White hydrogen

It is a type of hydrogen found in nature, usually in gaseous form ( $H_2$ ). It can sometimes be found in underground deposits.

#### 2.2.1.2 Gray/Brown/Black hydrogen

The most polluting of all is black or brown hydrogen, which is produced with bituminous coal or lignite, respectively, through a process known as gasification -coal is burned at very high temperatures. In this way, a gas is obtained from which the hydrogen is extracted.

Gray hydrogen is the most commonly used form of hydrogen in the world. Generally produced by various processes that use fossil fuels (primarily steam reforming of natural gas, coal gasification or separation from coke oven gas). It accounts for as much as 76% of the hydrogen produced in the world. However, the production process of gray hydrogen has significant carbon emissions that are not aligned with climate objectives. Emissions from gray hydrogen production amount to about 9 kgCO<sub>2</sub>eq/kg of hydrogen produced, plus an additional 25% from the raw material supply. This emission of 10-11 kgCO<sub>2</sub>eq/kgH<sub>2</sub> is not environmentally sustainable.

In summary, gray hydrogen is the most commonly used form of hydrogen, but its production process emits significant amounts of carbon emissions. To address this issue, blue hydrogen can be produced by capturing and storing carbon emissions during the production process of gray hydrogen, or green hydrogen can be produced using renewable energy sources. The use of blue or green hydrogen will be crucial in meeting climate objectives and transitioning towards a carbon-neutral economy.

#### 2.2.1.3 Blue hydrogen

Blue hydrogen is a term used to describe hydrogen generated from non-renewable sources with a low carbon footprint. The process involves the reforming of natural gas, sometimes referred to as turquoise hydrogen, with carbon dioxide capture. Carbon capture, utilisation, and storage (CCUS) is a process that captures carbon dioxide emissions from sources like coal-fired power plants and reuses or stores the emissions. CCUS focuses on capturing carbon emissions at the source, and then either

using them (carbon capture utilisation, CCU) or transporting them to a different location for storage (carbon capture storage, CCS).

CCUS is important because it has the potential to help lower the rate of CO<sub>2</sub> that is released into the atmosphere. It will be a vital aspect of helping the UK reach net zero by 2050.

The advantage of centralized hydrogen production from the reforming reaction is that carbon dioxide capture is more favorable than diffuse capture. Installing capture units at this point is cost-effective due to the high concentration of the compound and the economy of scale. Capturing carbon dioxide emissions from a combustion and distributed process is costly and inefficient. Hence, burning hydrogen obtained from natural gas, with captured carbon dioxide in reformers, is more environmentally efficient than directly burning natural gas in a distributed manner.

The most relevant process to obtain blue hydrogen is by reforming natural gas with carbon dioxide capture. Blue hydrogen is defined as hydrogen generated from non-renewable sources emitting less than 4.37 kgCO<sub>2</sub>eq/kgH<sub>2</sub> (36.4 CO<sub>2</sub>eq/MJ). To achieve a 60% reduction, it is only necessary to capture the reaction itself, and not other emissions associated with the process, such as the burning of fuel to achieve the necessary temperatures of the reformer.

Although the production of blue hydrogen through coal gasification is technically complex, it is possible to significantly reduce emissions from other fossil fuel processes. For example, the reforming or pyrolysis of natural gas, electrolysis with non-renewable electricity (nuclear, natural gas, mix), gasification (coal, waste mixture, plastics), thermal cracking (naphtha), or chlorine production (non-renewable electricity).

The adoption of blue hydrogen production has the potential to significantly reduce carbon emissions and promote sustainable development. Governments and industries need to invest in the development and implementation of blue hydrogen production technologies to mitigate the effects of climate change. However, blue hydrogen should not be viewed as a long-term solution, as it is still a non-renewable source of energy. Instead, efforts should be made to develop and adopt renewable energy sources, such as wind and solar power, to meet energy demands sustainably.

However, blue hydrogen, generated from non-renewable sources with a low carbon footprint, can significantly reduce carbon emissions when compared to other fossil fuel processes. Governments and industries should invest in the development and implementation of blue hydrogen production technologies to mitigate climate change.

In conclusion, blue hydrogen should not be viewed as a long-term solution, and efforts should be made to transition towards renewable energy sources.

#### *2.2.1.4 Orange/Amber hydrogen*

If the hydrogen obtained comes from non-biodegradable waste, avoiding a final destination with negative environmental impacts, such as incineration or landfilling, is called orange hydrogen. If we proceed to capture and store the CO<sub>2</sub> produced during the synthesis of orange hydrogen, we are facing amber hydrogen.

#### *2.2.1.5 Green hydrogen*

The production of green hydrogen can be done through various eligible processes, including water electrolysis, biogas refurbishment, reforming organic compounds, gasification, and chlorine production. While some of these processes, such as gasification, generate significant carbon dioxide emissions, Life Cycle Analysis only considers carbon dioxide emissions from fossil fuels. Biomass emissions are considered neutral, and the process of electrolysis of water does not emit any carbon dioxide directly.

Green hydrogen using renewable energy sources such as wind or solar power. This process involves splitting water molecules into hydrogen and oxygen using an electric current. The resulting hydrogen is considered "green" because it is produced using clean, renewable energy sources, and does not produce greenhouse gas emissions or other pollutants during the production process.

Green hydrogen has been identified as a key component in the transition to a low-carbon economy, as it can be used as a fuel for transportation, heating, and electricity generation without contributing to climate change. However, the production of green hydrogen is currently more expensive than other forms of hydrogen production, and

significant investments in renewable energy infrastructure will be necessary to scale up production and reduce costs.

Green hydrogen has the potential to reduce greenhouse gas emissions even more than blue hydrogen. While both types of hydrogen are produced with low carbon dioxide emissions, blue hydrogen requires the management of captured CO<sub>2</sub>. Green hydrogen avoids this, making it even more environmentally friendly.

One significant advantage of green hydrogen is its potential for large-scale production using renewable energy sources like wind, solar, hydraulic, and geothermal energy. Green hydrogen can be produced in any installation that generates renewable electricity and has water. This makes green hydrogen an important factor in furthering the deployment of renewable energy sources.

In summary, green hydrogen is a type of hydrogen that is obtained from renewable sources and has a low environmental impact. It is produced through water electrolysis and renewable electricity and has the potential to reduce greenhouse gas emissions even more than blue hydrogen. With its potential for large-scale production using renewable energy sources, green hydrogen is an important factor in furthering the deployment of renewable energy sources and reducing greenhouse gas emissions.

Green hydrogen has numerous benefits such as being a low-carbon fuel that can be produced from renewable sources, which can contribute to a more sustainable energy future. However, the high cost of production has been a major obstacle to its widespread adoption. Fortunately, the costs of production are decreasing rapidly due to technological advancements and increased investment in renewable energy.

#### 2.2.1.6 *Pink hydrogen*

Pink hydrogen is hydrogen that is obtained by electrolysis of nuclear-powered water. It's a fairly sustainable type of hydrogen.

#### 2.2.1.7 Turquoise hydrogen

Turquoise hydrogen is generated by pyrolysis of molten metal, fueled by natural gas. In the process, natural gas passes through a molten metal, releasing hydrogen and solid carbon, thus avoiding polluting CO emissions.

### 2.3 Hydrogen production

As it has been mentioned above, the most common method of producing renewable hydrogen is through water electrolysis, which involves the splitting of water molecules into hydrogen and oxygen using electricity. The electricity required for electrolysis can be generated from renewable sources such as solar, wind, hydro, or geothermal power. This makes the process environmentally friendly and sustainable.

Another route for producing renewable hydrogen is through the use of biomass or waste as feedstocks. This process, called biomass gasification or waste gasification, involves the thermal decomposition of organic matter to produce a gas mixture that can be further processed to generate hydrogen. This process is carbon neutral as the carbon dioxide produced during the process is offset by the carbon absorbed during the growth of the biomass or waste.

Renewable hydrogen can also be produced through the process of biophotolysis, which involves using photosynthetic organisms such as algae or bacteria to produce hydrogen from water and sunlight. This process is still in its early stages of development but has the potential to be highly efficient and sustainable.

#### 2.3.1 Electrolytic processes

Electrolysis of water is the decomposition of water into oxygen and hydrogen gas due to the passage of an electric current. This provides the necessary energy to break down a compound into its constituent elements. While electrolysis can be utilized for various substances to generate hydrogen (such as alcohols, certain acidic compounds, organic substances, etc.), the most crucial and extensively researched electrolytic processes involve water.



### 2.3.1.1 Photoelectrolysis

The typical method for generating electricity is by using solar radiation to power photovoltaic modules, which in turn supply energy to electrolyzers. However, in recent decades, significant attention has been devoted to developing materials that can enable reactors for producing hydrogen through solar activation.



In 2021, it was the 50<sup>th</sup> anniversary of Fujishima and Honda's seminal publication that identified certain materials capable of absorbing photons to produce electron-hole pairs, which can subsequently participate in oxidation-reduction reactions on the material's surface, either with or without a catalyst.

These pathways closely resemble those found in photosynthesis, and are generally referred to as artificial photosynthesis.

Despite the fact that photocatalysis has been recognized for more than a century, the major obstacle hindering its widespread use is the significant probability of product recombination, resulting in reduced conversion efficiency of solar energy into chemical energy.

Although various reactor configurations have been devised and promising results have been achieved in photoreduction of water to produce hydrogen and oxygen, the production efficiencies, such as solar-to-hydrogen (STH) ratio, are substantially lower than those obtained from other technologies.

As a result, this process's performance limitations have impeded its scaling up for industrial use.

In recent decades, an intermediate approach between photocatalysis and electrochemistry has been proposed to address the recombination mechanisms that occur when oxidation and reduction processes take place in close proximity on the photon-absorbing material's surface. This approach involves introducing the concept of a photoelectrode, which is similar in configuration to an alkaline electrolyser with its anode, cathode, and separation membrane between anolytes and catholytes.

The photoelectrode, in addition to handling the use of electrical energy for the "lysis" processes, is capable of absorbing photons, generating electron-hole pairs, directing these carriers towards the surface of the photoelectrode and the other electrode, and inducing the relevant catalytic reactions.

An intermediate pathway between photocatalysis and electrochemistry has been proposed in recent decades to avoid the recombination mechanisms that occur when the oxidation and reduction processes take place in close proximity on the surface of the photon-absorbing material.

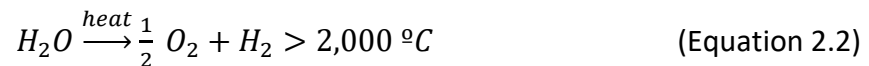
This pathway involves introducing the concept of a photoelectrode, which can manage the absorption of photons, generate electron-hole pairs, and induce catalytic reactions on the surface of the electrode. The direct input of photon energy from the illumination of the photoelectrode reduces the amount of electrical energy required for the lysis process, and in some cases, even eliminates the need for electrical energy altogether.

This technology is often referred to as "artificial leaves" and has shown promising results for the production of "solar hydrogen", with electrochemical efficiencies above 80%. While electrolyzers can operate 24 hours a day, photo-electrochemical systems can only operate during effective solar irradiation hours.

Additionally, while electrolyzers are centralized electrochemical systems that work at high current densities, photo-electrochemical systems are distributed electrochemical systems composed of many cells, as many as there are photovoltaic cells available.

### 2.3.1.2 *Thermolysis and Thermochemical cycles*

In photolysis and photocatalysis, the energy required to break the water molecules is acquired by directly absorbing photons. However, in thermochemical processes, the source of energy is heat. The high temperatures generate enough vibrational energy to break the water molecule, converting thermal energy into chemical energy. In the process of thermolysis, water is dissociated in a single step using heat sources with temperatures above 2,000°C. This method does not require any additional catalysts but may be less efficient and more expensive due to the high energy required to achieve the necessary temperatures.

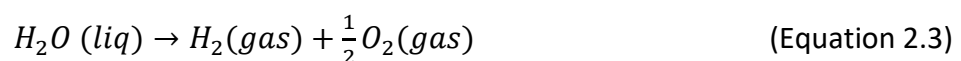


In order to achieve thermolysis, high temperatures must be reached without disrupting the energy balance. This is typically done in solar ovens which require expensive infrastructure, making it challenging to predict hydrogen production costs.

There are also thermochemical processes that involve cyclic endothermic and exothermic reactions where water is decomposed into hydrogen in several stages. The chemical compounds used in the reaction can be recycled except for water. Unlike thermolysis, this process doesn't need catalysis or membranes for O<sub>2</sub>/H<sub>2</sub> separation and operates at lower temperatures of about 300-900°C. However, the overall yield of the process is reduced due to the irreversibility associated with each stage.

### 2.3.1.3 *Electrolysis of water from electricity*

Electrolysis is a process that uses electricity to decompose water molecules and produce hydrogen and oxygen. This method is considered environmentally friendly as long as the electricity used comes from non-polluting sources. Currently, water electrolysis is the primary way of producing hydrogen using renewable energy. The process is versatile, modular, and can be easily integrated into different renewable energy production systems. It can also be used for both centralized and decentralized production, and allows for optimal management of micro-grids and smart grids. Electrolysis can be carried out at low or high temperatures using different technologies. The overall reaction of the process is the decomposition of water into hydrogen and oxygen as equation 2.7 shows.



To initiate the electrolysis reaction, a direct electric current is applied through a pair of electrodes connected to a power supply. One electrode, the anode, produces oxygen through the oxygen-producing half-reaction (OER), while the other electrode, the cathode, produces hydrogen through the hydrogen-producing half-reaction (HER). During the process, there is a transfer of electrons between the electrodes and the ions, with anions losing electrons to the anode and cations gaining electrons from the cathode. Since the electrolysis reaction is endothermic, it requires an external energy

input to occur ( $\Delta G > 0$ ), which can be provided in the form of electricity or heat. Assuming the reaction is reversible, the energy required can be calculated using the First Principle of Thermodynamics (Equation 2.8).

$$\Delta H = \Delta G + T - \Delta S \quad (\text{Equation 2.4})$$

Where  $\Delta H$  shows the total energy (enthalpy) that must be supplied in order to break the water molecule. This energy can have a thermal origin (entropy,  $T-\Delta S \equiv Q$ ) representing the irreversibilities of the system, or an electrical origin (free Gibbs energy,  $\Delta G$ ), since in an electrochemical process at constant pressure and temperature, all reversible work is electrical energy. At standard conditions ( $25^\circ\text{C}$ , 1 bar) these parameters take the following values:  $\Delta H_0 = 285.88 \text{ kJ/mol}$ ,  $\Delta G_0 = 237.23 \text{ kJ/mol}$  and  $T-\Delta S_0 = 48.65 \text{ kJ/mol}$ .

Figure 2-1 reflects the variation of the different terms in Equation 2.8 with respect to temperature. It can be seen that the electrical demand ( $\Delta G$ ) decreases as the temperature at which electrolysis takes place increases, the reduction being much more significant when the process occurs with water vapour than with liquid water. The abrupt change in  $\Delta H$  and  $T-\Delta S$  at  $100^\circ\text{C}$  is due to the vaporisation of water. As for the pressure, its influence on the total energy ( $\Delta H$ ) required for the process is not very noticeable.

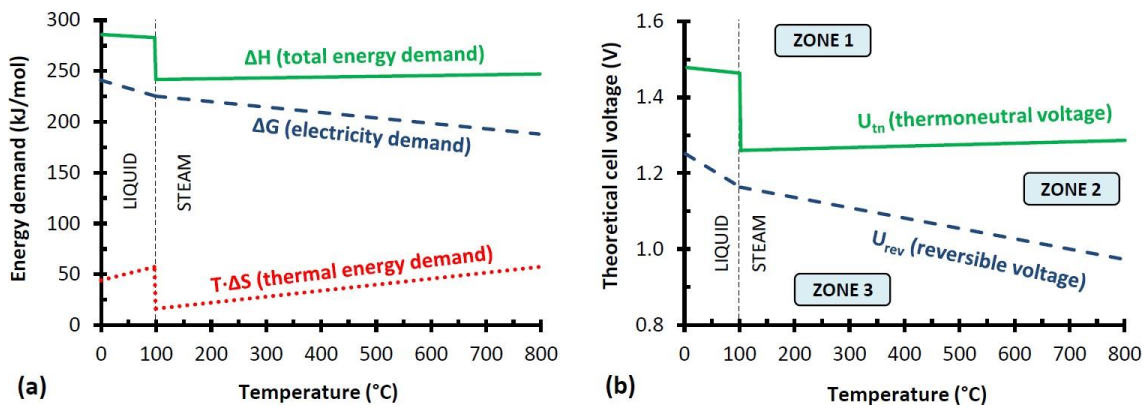


Figure 2-1. Thermodynamics of water electrolysis: (a) influence of temperature on thermodynamic parameters of water electrolysis at 1 bar; (b) dependence of reversible and thermoneutral voltage on temperature at 1 bar.

#### 2.3.1.3.1 Types of Electrolysis

There are two fundamental parameters that define the type of electrolysis carried out: temperature and pH. The dependence on temperature, as indicated above, strongly influences the potential necessary for electrolysis, since the reversible voltage tends to decrease as the thermal input ( $T\Delta S$ ) increases, following the dependence of the Gibbs free energy ( $\Delta G$ ) on temperature (see Figure 2-1a). Thus, depending on the temperature of the process, electrolysis can be carried out in two ways:

- At low temperature: in these processes, the operating temperature is usually 60-80 °C, so the electricity consumption is high, in the order of the energy contained in the hydrogen produced. This procedure is therefore only justified for on-site hydrogen production in small quantities and in the absence of other supplies, or for large-scale hydrogen production through integration with renewable energies, where a way of storing surplus renewable potential is sought.

With respect to pH, when water electrolysis takes place under neutral conditions (pH = 7), the theoretical potential difference between the oxygen (OER) and hydrogen (HER) production half-reactions is 1.23 V.

However, in the electrolysis process, the anode tends to acidify due to the generation of  $H^+$ , while the cathode alkalinises because  $OH^-$  groups are released. As a consequence, the pH around the anode and cathode varies, increasing the thermodynamic voltage of the process. For this reason, for an efficient process, concentrated solutions of  $H^+$  (acidic pH) or  $OH^-$  (basic pH) are required to avoid concentration overpotentials, as these are the most mobile ionic species. Although the characteristic potentials of each half-reaction vary in both basic and acidic media, the potential difference between anode and cathode is always the same. This allows us to define two ways of carrying out electrolysis at low temperature:

- Electrolysis in a basic medium: in these processes,  $OH^-$  ions are responsible for ionic transport. The electrolyte is usually a solution of KOH or NaOH. Anode and cathode are

separated by a porous medium (diaphragm) which prevents the gases generated at each electrode from mixing. This is the fundamental principle of alkaline electrolyses, historically the first technology to be developed, since in strongly basic media many metals are passivated and corrosion is prevented.

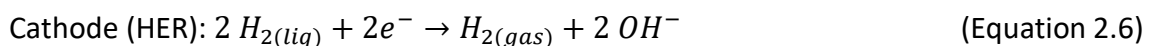
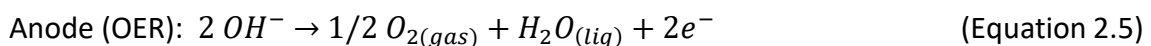
-Electrolysis in an acidic medium: in this case,  $H^+$  ions are responsible for ionic transport, so a solution of  $H_2SO_4$  or  $HCl$  can be used as electrolyte. However, electrolyzers using liquid acid electrolytes rarely exist due to severe corrosion problems. The development of a solid polymer electrolyte (SPE), where the  $H^+$  remain confined in the membrane electrolyte to ensure ionic transport and at the same time separate the gases, has allowed the development of this technology, using PEM (proton exchange membrane) electrolyzers.

- High temperature: in these processes, electricity consumption decreases considerably, although steam and a high temperature thermal source are required to carry out the process. The technology also needs to be modified to solid oxide in SOEC (solid oxide electrolysis cell) electrolyzers.

#### 2.3.1.3.1.1 Alkaline Electrolysis

An alkaline electrolysis cell, basically consists of two electrodes that are immersed in a liquid electrolyte (an aqueous alkaline solution, usually based on potassium hydroxide -  $KOH$ - or sodium hydroxide -  $NaOH$ -) and a porous diaphragm that acts as a separator between the cathodic and anodic chamber, which allows ionic transport ( $OH^-$ ), but is impermeable to gases.

When the potential difference between the electrodes occurs, semi-reactions take place simultaneously at the anode and cathode. At the cathode, the reduction reaction of water to hydrogen takes place, generating  $OH^-$  ions. The  $OH^-$  ions generated at the cathode move towards the anode (oxidation half-reaction), where they give up their electrons. The pressure in the anode and cathode compartments must be the same, which is vital to ensure the mechanical integrity of the diaphragm:



A general schematic of an alkaline electrolysis cell is made up of the following elements:

- Electrodes: these are responsible for conducting the electric current to the anode and cathode chambers. **The positive electrode** is called the anode and in its separation interface with the electrolyte, the semi-reaction of gaseous oxygen formation takes place, and in the negative electrode or cathode, the semi-reaction of gaseous hydrogen formation takes place. The requirements to be met by the electrodes are mainly high corrosion resistance, good electrical conductivity, large active area and structural integrity. The cathode is usually made of stainless steel, Ni or Ni-Raney, although Ru, Co or Mo alloys are sometimes used. The anode, on the other hand, is made of Ni or Ni-coated steel.

- Separating medium (diaphragm or membrane): the function of the separator is to divide the electrolysis cell into two chambers (anodic and cathodic compartment), allowing only OH<sup>-</sup> ions to pass between the two electrolytic chambers, and being impermeable to gases. Among these separating media, diaphragms are the most widely used elements to date. Initially they were made of asbestos, but as it is a carcinogenic material, they have been replaced by new configurations. One of the most commonly used diaphragm materials is composed of a polysulphone network and zirconium oxide (ZrO<sub>2</sub>) as an inorganic filler, known as Zirfon® PERL, marketed by the company AGFA.

In recent years, attempts are being made to replace the diaphragm with an anion exchange membrane (AEM), thus eliminating the use of a corrosive liquid electrolyte such as NaOH or KOH solutions. The use of anion exchange membranes allows the electrodes to be fabricated directly on the membrane, enabling the development of new cell configurations (analogous to PEM electrolyzers, as will be discussed in later sections). These new designs aim to reduce the ohmic overpotentials associated with the diaphragms, achieving higher current densities and efficiencies. However, an AEM with durable electrochemical and mechanical properties under alkaline conditions is not yet available.

- Electrolyte: provides the ions responsible for conduction inside the electrolytic cell. To minimise losses to the resistance of the electrolyte, solutions of KOH at around 30-35% or NaOH at 15-20% by weight are used, as values above or below these decrease the conductivity of the electrolyte. Since the conductivity of the electrolyte increases with

temperature, it is usually operated between 60-80 °C, i.e. below the boiling point of the aqueous solution.

Alkaline electrolysis is a very mature technology that is currently used on an industrial scale, with commercially available equipment offering very high hydrogen production capacities in the MW range.

The key advantages of this technology are its proven durability, its maturity, its availability and its low specific costs (these are systems that are not based on components containing noble metals) compared to other technologies. Disadvantages are mainly the low current densities and the use of a highly corrosive liquid electrolyte.

In general, these commercial systems usually operate at temperatures between 65-90 °C and pressures typically around 10-30 bar, although equipment operating at atmospheric pressure is also available.

The purity level of the hydrogen produced is around 99.5-99.9 % vol., because the gases generated at the anode and cathode can easily diffuse through the porous diaphragm used as a separator, so if higher purity hydrogen is required, it is necessary to incorporate a purification stage based on de-oxo reactors, capable of removing traces of oxygen, raising the purity to >99.999%.

The overall efficiencies of these systems are in the range of 55-65 % with respect to the LHV (Low Heating Value) of the hydrogen produced, when operating at nominal conditions between 0.25-0.45 A/cm<sup>2</sup>. Hydrogen production is limited in practice to an operating range of 20-100% of nominal performance to prevent the formation of flammable mixtures due to gas diffusion through the diaphragm which occurs mostly at low current densities (< 0.1 A/cm<sup>2</sup>).

With regard to the durability of the systems, commercial equipment currently offers around 95,000 hours of operation, with typical degradation ratios of 1-3 μV/h, which adequately meets industrial requirements (25 years of operation). However, these systems are highly influenced by work with variable loads. The operation against dynamic loads, together with more frequent shutdowns and ignitions, reduce the durability of the same, decreasing the quality of the gas obtained and reaching lower efficiencies.



Currently, R&D efforts in this technology are mainly aimed at solving the major disadvantages of this type of electrolysis, which are the low current density and the problems derived when working in dynamic conditions. So future challenges go through:

- Development of advanced materials to improve catalytic activity in electrodes, reducing overpotential for both cathodic and anodic reaction. In the same sense, all those advances that allow to minimize the manufacturing costs of the electrodes are important, facing the scaling of electrolysis systems at the scale of MW, with stack of larger diameters and number of cells.

- Optimization of the space between the electrodes to reduce ohmic losses and increase the current density of the process. Currently, the distance between the electrodes is usually below 1 mm, using in many configurations a zero-gap cell design where space is minimized, since the electrodes are in direct contact with the diaphragm. However, these configurations can limit the output of the generated gases because there is so little space between electrodes, and new designs are needed to improve the flow distribution.

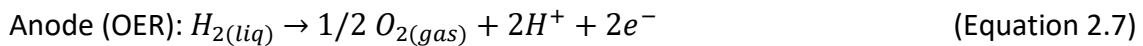
- Development of anionic exchange membranes (AEM) as separators in the electrolysis cell, thus eliminating the use of a liquid electrolyte. This type of membrane will reduce the ohmic overpotentials associated with the separating medium currently used (diaphragms), achieve higher current densities and decrease the diffusion (crossover) between the anode and cathodic chamber

#### 2.3.1.3.1.2 PEM Electrolysis

A **Proton Exchange Membrane (PEM)** type water electrolyser is an electrochemical device where the reaction of water dissociation in hydrogen and oxygen is performed according to Equation 2.7. The energy required for this process is obtained by the passage of electric current through two electrodes, which are separated by means of a solid electrolyte. Thanks to the use of these PEM, the construction of this type of electrolyser is simpler than in alkaline electrolysers and its operation response is faster, so they are more compact and of lower volume.

The fed water flows through the channels, oxidizing at the anode to release  $O_2$  and  $H^+$ . This reaction is known as the oxygen evolution reaction (OER), according to the Equation 2.11. The  $H^+$  ions formed then flow through the membrane, and the electrons on the

other hand, circulate through the external circuit to the cathode, closing the electrical circuit that supplies potential to carry out the process. In the cathode, the protons that reach through the ion exchange membrane are chemisorbed in the electrocatalyst. These recombine with the electrons coming through the outer circuit, thus forming the hydrogen molecules, which are released as gas. This reaction is known as the hydrogen evolution reaction (HER), according to Equation 2.8:



Water electrolysis based on PEM technology offers a number of advantages for the electrolytic production of H<sub>2</sub> and O<sub>2</sub>, among which: possibility of working at high current densities, high purity of the obtained H<sub>2</sub> (> 99.99%), possibility to produce gases at high pressure in the installation without additional energy input, faster response to variable power supply (such as renewables) and use of a solid electrolyte (PEM) which involves not having to manage a liquid electrolyte as in the case of alkaline technology. The biggest drawback of these systems is their cost, due to the use of precious metals as catalysts, and the strongly acidic environment to which materials are exposed

A PEM electrolysis cell is formed by a polymer membrane submerged in an aqueous solution that separates the cathodic and anodic semi-cells. The electrodes, which are carriers of the catalytic layers and can be directly deposited on the membrane or on the current and flow distributors (a series of porous metal parts known as GDL, gas diffusion layer) form together with the membrane, the MEA (membrane electrode assembly), which is the heart of a PEM electrolyser. It is in this component that the electrolysis of water is performed, generating hydrogen on the one hand and oxygen on the other.

On both sides of the MEA and of the current and flow distributors (water/gas), a series of metal plates (known as bipolar plates) are located where the flow distribution channels are machined, responsible for distributing the water and carrying the generated hydrogen and oxygen to the outlet.

In a PEM electrolysis cell all these elements are mechanically supported by the terminal plates which together with the seals and the closing elements allow the anodic and

cathodic chambers to remain separated avoiding the contact between oxygen and hydrogen generated.

Each of the main components that make up an PEM cell is described below:

- MEA consists of membrane-electrode assembly (anode and cathode), the membrane being the central part of the assembly. It can be designed in different ways, although the difference is based primarily on where the catalytic layer is deposited: on the membrane or on the water and gas distribution layers (GDL).

- The main function of the electrodes is to facilitate contact between reagents and catalytic sites, for which it is necessary to facilitate the conduction of electrons and protons, the evacuation of gas products from the reaction and the arrival of water to the catalytic points. The electrocatalytic function will be determined by the catalytic material, usually a metallic oxide deposited on a support with a high surface area. Electrodes are very complex structures and are an element that is being actively investigated for optimization in terms of price and development.

As discussed in previous sections, anodic semi-reaction promotes oxygen evolution (OER), while cathodic promotes hydrogen evolution (HER). The OER reaction is the one with the slowest kinetics so this is the limiting reaction of the process. Therefore, stable electrocatalysts, with high catalytic and selective activities, are highly necessary to promote OER. Thus, the Ir or the Ru are the most used elements today for the synthesis of OER catalysts. For cathode HER, platinum has traditionally been used as a catalyst.

- The current distributors or diffusers of water and gas (GDL) are porous metallic grids that do not participate in the reactions and have the function of getting the current, transporting it from the bipolar plates to the MEA, also ensuring homogeneous access of water to the membrane and the removal of product gas.

The porosity of this material is an important factor: if the pores are too small they can cause problems in the transport of water and gas; if the porosity increases, the evacuation of gases is facilitated, but significant ohmic losses are introduced at the contact points between GDL and MEA, and between GDL and bipolar plaque.

Ti, in the form of a mesh or sponge, is the most commonly used material, as pores between particles allow gas and water to flow through it, while offering a large surface of contact with electrodes, which confers a greater conductivity.

-Bipolar plates constitute approximately 30% of the size and 50% of the total cost of a cell, so a good design for this component is essential. They are located at the ends of each cell and have machined a series of channels, which allow the entry of water to the MEA and the output of the generated gases.

Bipolar plates and flow distribution channels in PEM electrolysis cells: (a) main types of channel designs (coil, grid, parallel); (b) flow distribution and hydrogen fraction when using straight parallel **channels**.

They are essential in stack configuration as they connect cells in series (the anode of one cell connects to the cathode of the next) so that the correct functionality of the stack is guaranteed. Since materials with high corrosion resistance and high electrical conductivity are needed, noble metals with specific coatings are usually used. However, it is necessary to search for new alternatives for the manufacture of bipolar plates that improve corrosion resistance characteristics and have high conductivity, at lower prices.

Finally, as in other electrolytic technologies, several cells can be joined together, usually in series (bipolar, as in the case of alkaline electrolyzers), to form a stack or stacking, thereby increasing the total amount of hydrogen produced.

To properly service the stack, there must be a series of auxiliary systems that allow control of the operating parameters, maximize its efficiency and make it work safely. Similar to an alkaline electrolyser, these elements constitute the plant balance (BoP). Some examples are shown in Figure 2.2.



Figure 2-2. Examples of BoP for PEM electrolysis: (left) SMART ENERGIES CETH2 E5; (right) SIEMENS SILYZER 300.

For the development of PEM electrolysis it is necessary to achieve maximum efficiency at the lowest possible cost. This parameter is related to the amount of power supplied to generate a certain amount of hydrogen.

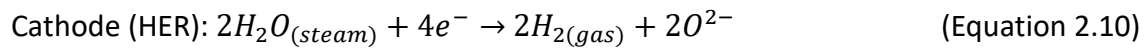
Since 2010, PEM electrolysis systems have followed a downward trend in system-wide energy consumption (kWh/kg), that is, efficiency in hydrogen generation has progressively improved. The advances in this specific technology have reduced the electric consumption in hydrogen production. In this way, the economic parameters have improved and this helps the viability of the process. Estimates for 2030 state that it will be possible to reach energy consumption values around 45 kWh/kg H<sub>2</sub>.

However, the efficiency of an PEM electrolyser is also affected by the voltage degradation, which refers to the increase in overpotential that must be applied to an electrolysis cell, in order to maintain constant hydrogen production. These effects are linked to several degradation processes, mainly in the catalytic layer and membrane, which increase the electrical resistance of the cell. Degradation is estimated to reach 4-8  $\mu\text{V/h}$  of operation. According to data from different manufacturers of PEM electrolysers, the reported durability is around 75,000 hours of operation.

#### 2.3.1.3.1.3 SOEC Electrolysis

Solid oxide electrolysis (SOEC) cells are devices that replace part of the electrical energy required to divide water with thermal energy. A SOEC cell is structurally similar to a solid oxide fuel cell (SOFC) that works in reverse. In these cells, the cathode is fed with water

vapor, which is reduced by H<sub>2</sub> and O<sub>2</sub><sup>-</sup>. The oxide ions then migrate through an anionic electrolyte to the anode where they are oxidized to produce O<sub>2</sub>:



The use of higher temperatures (600-1000 °C) increases the efficiency of the electrolyser by decreasing the process's overpotentials, allowing the cell to even run below the thermoneutral voltage. However, it is necessary to have water vapour and a high temperature thermal source to carry out the process, which can sometimes limit the applications of this technology.

Another advantage of SOEC units is the use of a solid electrolyte which, unlike alkaline systems, is non-corrosive and does not experience problems related to liquid/gas distribution (as in low temperature electrolysis) because it works with temperatures well above the water vaporization point. In addition, at such high temperatures, the need for electrocatalysts is less significant compared to low temperature requirements, making it possible to operate without the use of precious metals as catalysts.

As discussed above, the components of a SOEC electrolysis cell must be resistant to the high temperatures that occur in these processes. For this reason, the materials of a SOEC cell are usually ceramic:

- The solid electrolyte generally consists of a mixed oxide based on zirconium oxide stabilized with yttrium oxide (ZrO<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub>), generally known as YSZ (yttria-stabilized zirconia), which acts as a ceramic membrane. The transport of oxide ions occurs through it by diffusion through the crystalline structure. The electrodes are then placed on both surfaces of this ceramic membrane.

- Electrodes must be highly porous ceramic materials capable of conducting electrons and facilitating mass transport (hydrogen and oxygen), as well as being a good ionic conductor to enable migration of O<sub>2</sub>-species.

The cathode composition (HER) is mainly based on a ceramic-metal alloy (cermet) containing Ni and Zr (usually in the form of Ni/YSZ). For the anode (OER), materials usually consist of mixed oxides with a perovskite type structure (ABO<sub>3</sub>). To this end, the

combination of different metals with different levels of doping have been developed with the aim of improving the stability and activity of these components. Lanthanum manganite doped with strontium (LSM) is considered as the reference compound, as it is particularly suitable for operations above 800 °C. However, as it is a purely electronic conductor, it is usually mixed with YSZ (the material used as an electrolyte), to form an LSM-YSZ compound, which presents a good conductivity, both ionic, and electrical.

-The cell also has interconnectors, which serve to transport the electric current, ensure the distribution of gas in each cell and act as a separator between the anode of a cell and the cathode of the adjacent (similar to bipolar plates in an PEM cell).

Therefore, it must be made of a material with excellent electrical conductivity and high corrosion resistance. Another important feature that interconnectors must comply with is related to their mechanical properties. Since these elements join different cells, they must avoid breaking them during their operation, so materials used as interconnectors must have thermal expansion coefficients comparable to the rest of ceramic elements. But they must also be malleable enough to be stamped, cut or machined.

The use of some types of stainless steels, with certain modifications and/or coatings (since certain elements that make up these steels, can migrate and deactivate electrodes), can offer the necessary characteristics in SOEC.

Finally point out that SOEC cells can have different geometries: flat (similar to other conventional electrolytic cells, such as in alkaline or PEM), tubular (where the electrolyte has the shape of a thin-walled tube) and even more complex configurations, like a honeycomb.

An example of a SOEC electrolyser consisting of 24 flat cells, as well as a simplified operating scheme, with different sub-systems that allow the equipment to work correctly (BoP), analogous to alkaline electrolysis and PEM. As can be seen, a high temperature source (HT) is necessary to start the electrolysis process.

SOEC electrolyzers are the most electrically efficient, but it is the least developed electrolysis technology. A major challenge is the hydrogen production by electrolysis at high temperatures, which require the use of expensive materials and more complex manufacturing methods. The different components of the cell may have different

coefficients of thermal expansion, so the start/off cycles are harmful for interfacial contact between the electrodes and the electrolyte, leading to delamination of the different layers and increasing the internal resistance of the cell. In addition, to increase the driving properties, the different components must be very thin, which makes them very fragile, causing the assembly of the cell to be very complex. For these reasons, before this technology can reach commercial deployment, numerous investigations must still be dedicated to optimize materials, components and systems.

However, this technology has great potential for hydrogen production by harnessing energy generated from different thermal sources, such as solar concentrating plants, geothermal or nuclear reactors. In addition, since a SOEC cell is essentially a solid oxide fuel cell that works in reverse, it opens the possibility of using reversible devices that can function as an electrolyser or fuel cell.

Finally, the overall efficiency of SOEC technology can be improved by co-electrolysis processes, with water vapor and carbon dioxide to produce synthesis gas ( $H_2 + CO$ ), of great industrial interest for the production of different synthetic fuels.

## **2.4 Hydrogen: Storage, Transportation and Transformation**

### **2.4.1 Hydrogen storage**

One important property of hydrogen, particularly when it comes to storage, is its gravimetric energy density. One kilogram of hydrogen can transport 33.3 kWh/kg (LHV) of energy. However, its volumetric storage density at ambient pressure is only 3 Wh/l, which is a major limitation. To address this issue, hydrogen is often stored as a gas at extremely high pressures (up to 700 bar, known as Compressed Gaseous Hydrogen or CGH<sub>2</sub>) or as a liquid at very low temperatures (-253 °C, known as Liquid Hydrogen or LH<sub>2</sub>) and low pressure. Additionally, combining hydrogen with other elements or compounds can help alleviate the problem of its low volumetric density.

H<sub>2</sub> storage alternatives can be classified into two main groups:

- Physical storage techniques: in which H<sub>2</sub> is conserved in molecular form while its temperature and pressure conditions are varied.



- Chemical storage techniques: in which  $H_2$  binds to another element through covalent or ionic bonds, resulting in compounds with chemical properties different from those of  $H_2$  and more favorable for storage. Within this second group, the two main alternatives are based on:

- Union of  $H_2$  with an organic compound to form a hydrogenated organic compound.
- $H_2$  bonding with a metal to give a metal hydride.

#### 2.4.1.1 Physical Storage

Physical storage refers, in general terms, to the use of a tank or deposit to contain  $H_2$  in its molecular form, varying its pressure and temperature conditions to achieve a favorable volumetric density.

- **Compressed Hydrogen**

Storing hydrogen in pressurized cylinders is the most straightforward and commonly used method for storing small amounts of gas. Many companies supply cylinders in various sizes, and hydrogen is typically used as a chemical agent in analytical or production processes. Compressed hydrogen is mainly used for onboard vehicle storage at high-pressure refueling stations (825-950 bar). For instance, in the hydrogen tank (156L) in Hynday Nexa it is possible to compress 6,3kg of  $H_2$ .

However, the energy required for compression is significant, accounting for approximately 7% of the hydrogen energy content. To address this issue, storage of hydrogen in geological formations such as salt caverns, aquifers, depleted oil and gas fields, hard rock caverns, and coal seams has been considered as a potential solution. This large-scale storage method can store vast amounts of energy in the form of hydrogen underground at high pressure, resulting in high energy densities. Gas immobilization mechanisms such as structural/stratigraphy, residual/capillary, mineral, and dissolution trapping or adsorption trapping in the case of coal seams are employed to accomplish this large-scale storage.

- **Liquid Hydrogen**

Cryogenic liquefaction is the process of turning a gas into a liquid by cooling it to a very low temperature (<150 K) at atmospheric pressure. This process is used for permanent gases such as He, H<sub>2</sub>, neon, N<sub>2</sub> and O<sub>2</sub>. Liquefied hydrogen solves the problem of its low storage capacity, but it requires complex technology and infrastructure due to its very low boiling point and low latent heat.

Cryogenic tanks are used to store the liquefied hydrogen, with thermal insulation technology designed to minimize evaporation. The tanks are typically cylindrical and can be placed horizontally or vertically, or even spherical for larger applications. The daily boiling rate is low for modern large-scale cryogenic tanks, but the hydrogen cannot be stored for long periods without a cooling system.

- **Cryo-Compressed Hydrogen**

The cryo-compression technology combines high pressure and low temperature to store energy more efficiently. This method can be applied to H<sub>2</sub>, and it offers several advantages over conventional storage systems. However, it is still in the early stages of development, and more research is necessary. Cryo-compression technology allows for the use of compressed LH<sub>2</sub> or H<sub>2</sub>, depending on availability and cost, and it reduces the cost of liquefaction and minimizes the boil-off of H<sub>2</sub> during vehicle use.

#### 2.4.1.2 Chemical Storage

Hydrogen can form compounds with other elements that offer better storage conditions than pure hydrogen due to their higher density. These compounds can be solid, liquid or gas. Releasing hydrogen from these compounds (dehydrogenation) usually requires energy, while binding hydrogen to form these compounds (hydrogenation) usually releases energy. Organic liquids (LOHC) and metal hydrides are examples of chemical compounds that have been studied for hydrogen storage. The type of storage chosen depends on the specific application and whether regeneration of the storage system is necessary.

For large-scale transport, indoor hydrogenation and external dehydrogenation may be necessary.



- **Organic Liquids (LOHC)**

LOHC systems are composed of pairs of organic compounds, the hydrophobic compound being typically an aromatic or heteroaromatic compound, and the hydrophilic compound rich in hydrogen, typically a cyclic or heterocyclic compound. LOHC is loaded with hydrogen analogously with catalytic hydrogenation reactions. The conditions required for exothermic hydrogenation are pressures of 1 to 5 MPa and temperatures of 373 to 523 K. Typical hydrogenation catalysts are Ni or Ru on oxide supports placed in reactors.

The conditions required for endothermic dehydrogenation are pressures of 1 to 0.5 MPa and temperatures of 423 to 673K. Normally, dehydrogenation catalysts are Pt or Pd, although other compounds such as Ru are beginning to be used, on oxide supports placed in tubular reactors. Research on LOHC began focusing primarily on cycloalkanes for their high hydrogen storage capacity (6-8%w/w). Subsequently, the heterocyclic aromatic compounds (N- Heterocycles) were also considered appropriate for this task. Recently, N-ethylcarbazole (NEC), dibenciltoluene and formic acid have been suggested as H<sub>2</sub> storage materials for their more favorable properties. Already used industrially as a heat transfer fluid, dibenciltoluene is in a liquid state over a wide temperature range (boiling point 390°C) and has a hydrogen storage density of 6.2% by weight of H<sub>2</sub>. Formic acid (FA) has a capacity of 4.4% w/w hydrogen.

- **Metal Hydrides**

Metal hydride technology involves the chemical storage of H<sub>2</sub> in solid form through an adsorption process using certain materials such as metals and intermetallic alloys. This allows for the storage of large quantities of H<sub>2</sub> with high volumetric density, low cost, and safety at low temperatures and fuel cell pressures. However, there are several issues associated with metal hydrides as a hydrogen storage system, including low reaction kinetics, low reversibility, and high dehydrogenation temperature.

Furthermore, metal hydrides can be heavy, leading to a reduction in the power/weight ratio in automobiles. Although there are more than 2,000 elements, compounds, and alloys that form hydrides, no storage system has met all the

objectives set by the DOE, particularly in automotive applications. This is due to the dilemma of low dehydrogenation temperature with irreversible storage or high dehydrogenation temperature with reversible storage. Hydrogen dissolves in the metal phase with increasing pressure at a given temperature, while the alpha phase becomes the hydride phase as the temperature rises.

The pressure increased leads to less and less hydrogen content until the material is charged, and heat must be supplied in the discharge to maintain reversibility conditions. However, even in the best cases, a hysteresis effect occurs.

## 2.4.2 Transportation

After production, hydrogen needs to be transported to the end-user. There are three main methods of transporting hydrogen, which are similar to those used in the natural gas industry: by sea for long distances or remote areas, by tanker trucks or cylinders for shorter distances on land, and through pipelines.

### 2.4.2.1 Maritime Transport

Transporting hydrogen by sea offers several advantages, including the ability to cover long distances and reach isolated areas, diversify hydrogen supply and export countries, and promote the generation of hydrogen from renewable energies in favorable locations and exporting it to countries with high energy demand.

The strategy for hydrogen transport by ship is similar to that of liquefied natural gas (LNG) transport, requiring liquefaction ( $LH_2$ ) and regasification at the receiving point. However, the necessary infrastructure for maritime transport is expensive, and the design of ship insulation is a significant technological challenge due to the high temperature difference between the liquid and the outside. Liquid hydrogen is stored at  $-253^\circ\text{C}$ , while liquefied natural gas is stored at  $-161^\circ\text{C}$  and liquefied petroleum gases are stored at room temperature.

**Liquid Organic Hydrogen Carrier (LOHC)** technology offers an alternative solution to transporting hydrogen without the need for compression, making it safer, more practical, and cost-efficient for maritime transport. LOHC technology chemically bonds hydrogen to a stable organic liquid carrier, such as toluene, which is converted to



methylcyclohexane and easily transported and stored at ambient temperature and atmospheric pressure. Another method for transporting hydrogen is through ammonia, which is already produced and transported globally as a commodity.

Ammonia is synthesized from hydrogen and nitrogen using the Haber-Bosch process and is a favored method for transporting hydrogen over long distances due to its lower energy storage costs compared to hydrogen. Additionally, ammonia already has a global infrastructure in place for transportation and storage as it is widely used as a fertilizer. Lastly, existing standards already regulate its production, transport, and use due to its high usage.

#### *2.4.2.2 Land Transport*

To distribute hydrogen over short distances (<300 km), trucks are used, although rail could also be a potential option. However, the current structure of distribution through trucks meets specific industrial needs, and is not yet prepared for widespread use as a future energy carrier due to its energy inefficiency. Land transport requires a higher amount of associated material and consumes more energy to transport hydrogen.

The lightness of hydrogen gas impacts the cost and energy efficiency of its land transport, as it needs to be compressed at high pressures or liquefied to increase the amount transported in a reasonable volume.

#### *2.4.2.3 Current gas network and specific hydrogen network*

The most feasible method for widespread hydrogen transport is through a pipeline network, but it requires a high initial investment and large and continuous quantities of hydrogen to be transported to be profitable. Blending hydrogen into existing natural gas pipeline networks has been proposed as a cost-effective means of delivering hydrogen to markets during the early development phase. This method has been used in the past to distribute hydrogen-rich gas to households in some countries through gas pipelines, but only over short distances and reduced shares. Adding hydrogen to natural gas networks has been considered by many countries, and it can be done without negatively impacting end users or the pipeline infrastructure up to 5-15 %vol hydrogen.

The text discusses the feasibility of adding hydrogen to natural gas networks for distribution. Up to 10 %vol hydrogen can be transported in existing networks without damage, but some components may be unsuitable.

The chemical properties of hydrogen differ from those of natural gas, especially in density, reactivity, calorific value, ignition energy, flammability and combustion rate. The introduction of hydrogen into the gas network entails a clear change in the composition of the product transported and delivered to the customer. In this direction, state regulations limit the mixing of hydrogen in the gas network to certain percentages. The introduction of hydrogen presents some uncertainties, as it can damage the transport network and have undesirable effects on equipment using gas.

The permitted concentration of hydrogen in the network varies significantly between Member States of the European Union (between 0.1-10 %vol), and in a large number of countries injection is not yet permitted. Neither international nor European standards define rules for the permissible concentration of hydrogen in the natural gas network.

Larger additions may require expensive conversions of appliances. Many gas transport networks and storage facilities that were used in the past are still in use today and could store significant amounts of hydrogen. The conversion of existing natural gas networks to hydrogen has been explored in some regions, such as Leeds in the UK. In Europe, the development of a specific hydrogen network is currently being considered and studied.

## **2.5 Technologies of use of Hydrogen**

Hydrogen has various applications and can be classified into two broad categories.

The first category is using hydrogen as a feedstock, a role that has been recognized and will continue to evolve.

The second category is using hydrogen as an energy carrier to enable the energy transition, which has already started and is expected to grow significantly in the future as it was commented in point 2.1.1.

Due to its versatility and multiple uses, hydrogen can help decarbonize existing economies using different technologies.

### 2.5.1 Fuel cells

Fuel cells are devices that can convert the chemical energy of fuel directly into heat and electricity through an electrochemical process. They consist of an electrolyte and two electrodes, an anode and a cathode. Fuel cells are capable of continuous power generation because they allow for the replenishment of consumed reagents, unlike batteries which have limited energy storage. The process involves the transformation of hydrogen and oxygen into water while producing electricity.



Electrochemical reactions occur on the surface of the electrodes where the fuel is oxidized at the anode and the oxygen is reduced at the cathode. The electrolyte acts as an ionic conductor and electrical and gas insulator.

These systems have several benefits including high electricity production efficiency, no noise due to the absence of moving parts, modularity, flexibility enabling their use for distributed generation, cogeneration, and transportation.

There are many types of fuel cells that can be classified mainly according to the type of electrolyte used and the operating temperature:

#### 2.5.1.1 Proton exchange membrane fuel cells (PEMFC)

The solid polymer electrolyte used in these batteries is typically NAFION and facilitates proton exchange. These batteries operate at low temperatures, around 80°C, which results in slow reaction speeds. Consequently, sophisticated and costly catalysts such as finely divided platinum electrodes are required. Additionally, these batteries need to be supplied with highly pure hydrogen to avoid poisoning the catalysts by CO. To address this issue, direct methanol fuel cells have been proposed as an alternative to hydrogen-powered PEMs. Although energy yields from PEMs are low, they are advantageous for use in portable devices, which are becoming increasingly popular in the transportation industry.

#### 2.5.1.2 Alkaline fuel cell (AFC)

These fuel cells were initially developed for the US space program and use liquid electrolyte, typically potassium hydroxide solution, and less complex metal electrodes. They usually operate at temperatures ranging from 100°C to 250°C, and there are newer designs that can operate at temperatures below 70 °C. The major drawback of this type of fuel cell is its susceptibility to CO<sub>2</sub> emissions, and its cost is also high. To become economically feasible, the fuel cell would have to increase its lifespan from 8.000 to 40.000 hours.

#### 2.5.1.3 Phosphoric acid fuel cells (PAFC)

These fuel cells utilize liquid phosphoric acid as the electrolyte and porous carbon electrodes that contain platinum as a catalyst. Despite the use of platinum, they are heavier and larger due to their lower energy efficiency compared to other fuel cell types, so they are primarily used in stationary applications, ships, and submarines. However, they are the second most commonly used type of fuel cell. One advantage they offer is their reduced sensitivity to CO.

#### 2.5.1.4 Fused carbonate fuel cells (MCFC)

MCFC fuel cells are a type of high-temperature fuel cell that operates at temperatures ranging from 600 to 700°C, and they use a molten carbonate salt mixture as an electrolyte. Since MCFC operates at high temperatures, it eliminates the need for expensive catalysts in electrodes, and its energy efficiency is high, making it less sensitive to CO. However, the main disadvantage is that the components have a short lifespan due to corrosion. MCFC fuel cells are mostly used for stationary applications.

#### 2.5.1.5 Solid oxide fuel cells (SOFC)

This type of battery operates at extremely high temperatures between 600-1000°C and uses a solid electrolyte. The high temperatures result in high energy yields, and costly catalysts are not required. They are not very sensitive to CO and can even use it as fuel. Combined cycles can be used to increase their efficiency up to 85%. However, they have a short lifespan due to high temperatures, and refrigeration is needed which makes



them expensive. They are also sensitive to  $\text{SO}_x$  and  $\text{NO}_x$  which can harm the most commonly used catalysts.

### **2.5.2 Burners**

Hydrogen can be used as a fuel for industrial applications such as glass or cement, and is expected to become more competitive from 2030. To replace specific natural gas burners and furnaces with hydrogen burners, different engineering factors need to be considered, including the Wobbe index, which measures the calorific value produced by different gases when combusting.

While hydrogen's Wobbe index value is lower than natural gas, it is still within the accepted range. However, the combustion rate of hydrogen is much higher, which requires a redesign of burners and more complex control. Catalytic boilers and heat pumps are two types of burners that can be used for domestic and industrial applications.

### **2.5.3 Turbines**

In the gas turbines internal combustion to produce mechanical energy through the expansion of gases was used. These gases generate a large amount of thermal energy in the form of hot gases, which can be recovered and used to generate water vapor in a steam turbine. This process, called a combined cycle, is an efficient way to generate electricity.

To reduce carbon dioxide emissions, most gas turbines now use a certain percentage of hydrogen mixed in with natural gas. This percentage is set to increase gradually over time, with the aim of achieving 100% hydrogen use in gas turbines by 2030. The combustion of hydrogen produces no carbon dioxide emissions, making it an environment friendly fuel for power generation.

However, there are technical challenges to using hydrogen mixtures in high proportions, mainly due to the higher combustion rate of hydrogen, which can cause flames to recoil within the combustion chamber, leading to pressure fluctuations and the generation of  $\text{NO}_x$  emissions. To address this issue, improvements are being made to the design of

turbines, specifically the nozzles of the injector. These improvements help reduce the low-speed zone and center the flame, thus improving the recoil effect.

The amount of hydrogen in the fuel can be measured based on volume, mass, or heat input. However, there is a significant difference in the required flow rate of hydrogen compared to natural gas due to their different energy densities. Hydrogen-powered devices require 3 times more fuel by volume than methane.

The calorific value of a gas, which is a measure of its energy content, is an important factor to consider when selecting a gas engine, turbine, or cogeneration plant. The efficiency of gas engines is usually given in terms of the gas's PCI. When hydrocarbon fuels are burned, some of the combustion product is water, which stores a small fraction of the energy released during combustion as latent vaporization heat. This energy can be recovered by condensing the water vapor back into liquid form in some applications.

In summary, the use of hydrogen mixtures in gas turbines is a promising approach to reducing carbon dioxide emissions and achieving a carbon-neutral economy by 2050. However, technical challenges associated with using hydrogen mixtures above 30% must be addressed to ensure safe and efficient operation.

## **2.6 End-uses and applications**

### **2.6.1 Hydrogen as a feedstock**

According to the International Energy Agency, the production of hydrogen has grown in the last few years to reach 100-120 million Mg in 2019, with 70 million Mg being produced in its pure form. The current demand for hydrogen is mainly driven by the manufacturing of ammonia for use in nitrogen fertilizers and other chemicals, which accounts for two thirds of the total demand. Hydrogen is also widely used in the petroleum refining industry for the production of fuels.

#### *2.6.1.1 Steel Industry*

Direct iron reduction (DRI) is a process used to make steel from iron ore, like magnetite or hematite, using a solid reducing agent (carbon) or a gaseous reducing agent

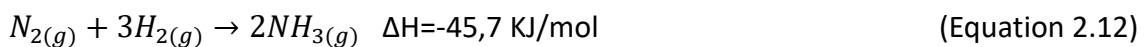
(hydrogen, synthesis gas) at lower temperatures than traditional blast furnaces (800-1200°C).

This process is the fourth largest source of hydrogen demand, accounting for 3% of total consumption, either in pure form or as a mixture of gases. As demand for steel is expected to increase by 6% by 2030, the interest in direct reduction processes is growing due to the steel sector's significant greenhouse gas emissions. By using renewable energy sources, this method can contribute to the electrification of the metallurgical sector. It takes an estimated 100 kg of hydrogen to produce 1 ton of steel. If the annual production of steel (1,800 Mt in 2018) had used the DRI process entirely with hydrogen, demand would have been 180 Mth<sub>2</sub> per year.

This could be a significant measure in reducing direct CO<sub>2</sub> emissions as one tonne of hydrogen can replace five Mg of coal (coke).

#### 2.6.1.2 Fertilizer

The Haber-Bosh process, which involves the synthesis of ammonia from nitrogen in the air and hydrogen, was first demonstrated in 1909 using a metallic catalyst at high pressure and temperature. The reaction is reversible and exothermic and requires 1.5 molecules of H<sub>2</sub> per ammonia formed.



Carl Bosch industrialized the process using iron catalysts, and the first operating plant was built in 1913. The ammonia produced can be neutralized with nitric acid to obtain ammonium nitrate, which revolutionized the agro-food industry by increasing the productivity of fields and helping to feed the growing world population. Nowadays, synthetic fertilizers represent about two-thirds of the fertilizers on the market, with ammonia production accounting for 27% of current hydrogen demand.

Around 80% of the world's ammonia production is used to synthesize fertilizers, and there are various products derived from ammonia synthesis used as input for agricultural nitrogen. The current food system of the planet is based on the use of nitrogen fertilizers, which has increased by 800% in recent decades. Several initiatives

have incorporated capture units or replaced green hydrogen reforming plants to decarbonize ammonia production.

#### 2.6.1.3 Refineries

Crude oil is a complex mixture of hydrocarbons containing impurities like sulfur, nitrogen, oxygen, and heavy metals such as iron, nickel, and vanadium. Refining the crude oil allows for the separation and classification of different hydrocarbon fractions, generating value-added products like gasoline, diesel, jet fuel, and lubricants.

Hydrogen is a vital component in refinery processes, especially hydrotreatment, which helps eliminate harmful products. This involves adding hydrogen to promote hydrogenation and hydrogenolysis reactions that saturate aromatic compounds or remove elements such as sulfur, nitrogen, or metals. Other reactive processes where hydrogen is a raw material include hydrodesulphurisation, hydroisomerization, dematerialization, and hydrocracking. The demand for hydrogen in refineries has been increasing over the years due to higher consumption of products, and it is expected to continue growing as the specifications for transport fuels require further reductions in sulfur content.

#### 2.6.1.4 Synthetic fuel production

Converting hydrogen into other products has a significant advantage in terms of increasing its energy density, which is particularly important for mobility applications. This means that a greater amount of fuel can be transported, thereby increasing the vehicle's range. Using liquids instead of gases can increase a fuel's energy density exponentially since liquids take up much less space than uncompressed gases.

Synthetic hydrocarbons, are hydrogen-based liquid fuels that include methanol, gasoline, kerosene, light diesel, and heavy diesel. These fuels are particularly suitable for the most difficult-to-electrify transportation sectors such as air and sea transport. However, when these liquid fuels are used in internal combustion engines, they only address the problem of net CO<sub>2</sub> emissions and not the issue of polluting emissions like NO<sub>x</sub> or carbon monoxide.

Aviation is the main market niche for liquid fuels since using hydrogen for maritime transport is more feasible.

#### *2.6.1.5 Chemical products*

The two most important basic chemicals obtained from hydrogen are ammonia (55 %) and methanol (10 %), in addition to all organic compounds produced in refineries by previously exposed hydrogenation reactions (25 %). Hydrogen is also used as a feedstock for other inorganic basic chemicals (for instance, ammonia, amines, aniline, cycloalkanes, hydrogen peroxide, saturated compounds and alcohols).

### **2.6.2 Transport and mobility**

Green hydrogen fuel contributes to the decarbonisation of the road transport sector. The main advantages of hydrogen fuel cell electric vehicles are the zero emission of CO<sub>2</sub> and pollutants.

#### *2.6.2.1 Road Transport*

Today, the clearest example of light hydrogen-based mobility is the fuel cell-powered electric car. Light fuel cell transport has, for the coming years, a very specific range of application when autonomies are required to justify a high initial investment. However, a more extensive long-term deployment is not ruled out, as various analyses suggest a clear reduction in the cost of the vehicle when manufactured in bulk.

In the case of buses, there is still a range of use for the electric vehicle (in cities with a significant deployment of chargers), where the vehicle can periodically perform brief recharging every 20 km, approximately, to ensure a range of autonomy of 16 hours of daily work (2 shifts), including air conditioning of the vehicle. Vehicles with higher tonnage or greater autonomy requirements, fuel cell vehicles are the most viable option. Buses or waste collection trucks, as vehicles that always operate in a closed and known circuit always returning to the same base, are an ideal case to boost the hydropower infrastructure with a minimum investment, which allows a significant fleet of vehicles to be deployed.

In the case of HGVs, there is a high potential for the adoption of hydrogen fuel cell technology, since its requirements of high autonomies and high fuel consumption makes the alternatives for decarbonization are reduced. While for the transport of light cargo over short distances or low speeds you can think of hybrid vehicles, or even electric in some specific cases.

Other vehicles of great interest are waste collection trucks, given their particular characteristics and use. These vehicles have a certain duality in their daily journeys: urban collection at low speed and road transport at higher speeds. They have high fuel consumption due to waste lifting and compression machinery, which has led in many cases to the development of dual solutions based on hybrid trucks, where the fuel cell is used only for machinery or as a solution to increase autonomy. The transition of these vehicles to solutions based on electric motor, either by battery or fuel cell, has a high social acceptance and by municipal officials, not only for their contribution to environmental improvement, but also because it is a quieter solution, since noise is one of the main handicaps of this type of vehicle, usually driven by diesel combustion engines. A variant halfway between this type of vehicles and trucks, are street sweeping (sweepers), including examples of vehicles powered and fuelled entirely by fuel cells, and others where the battery only contributes to the movement of brooms and the suction pump, there are also hydrogen-powered motorcycles and bicycles.

#### 2.6.2.2 *Maritime Transport*

Maritime applications of hydrogen have already been tested in propulsion of medium and small-scale vessels, including ferris, but the reality is that its commercial deployment is still at a very early stage. There are exceptions, such as the Baltic area or the North Sea, where some countries have begun to regulate ferries to require them to be powered by 100% renewable energy, which has promoted the emergence of fuel cell powered vessels.

The development of new fuels will require the supply of renewable hydrogen for their manufacture as in the case of methanol or ammonia.

### 2.6.2.3 *Railway Transport*

The future potential of the hydrogen fuel cell train lies on new routes or on non-electrified routes. It is difficult to imagine that the hydrogen train will replace the thousands of km of electrified rail transport that already exist, but it does represent an opportunity to generate new routes at a cheaper cost than electrification, as in urban areas.

One of the first demonstrations has taken place in Germany, where Alstom has developed the train called Coradia iLint. Since 2018 it has operated the passenger route between the cities of Cuxhaven, Bremerhaven, Bremervörde and Buxtehude in Lower Saxony, and dozens of units. Alstom has also deployed trains in the UK to assess its competitiveness with regard to electrification, although this will depend on the price of fuel, although some studies already place it as a competitive option in terms of total cost. The use of the hydrogen train is not unique to Europe, as there are some experiences also in China, where Ballard has developed its model called FCveloCity, used for light trains such as trams.

Prior to this, in Asturias (Spain) a project was carried out in 2011 for the construction of a tram with a capacity for 20-30 passengers. Its main components were 4 engines, 2 fuel cells of 12 kW each, lithium-ion batteries, supercapacitors and a rack of 12 hydrogen bottles.

### 2.6.2.4 *Air Transport*

The use of hydrogen as a fuel in air transport is a promising technology that can help reduce greenhouse gas emissions and reduce dependence on oil.

However, the implementation of hydrogen as a fuel in aviation presents some challenges. One of the main challenges is that hydrogen has a lower energy density than traditional aviation fuel, which means that more volume of hydrogen is needed to provide the same amount of energy. This can increase the size and weight of the fuel tanks, which in turn can reduce the payload of the aircraft.

Another challenge is security. Hydrogen is highly flammable and requires additional safety measures for storage, handling and transport. In addition, hydrogen combustion



engines need to be adapted or designed from scratch, which increases development and production costs.

Despite these challenges, research and testing are under way to assess the viability of hydrogen as a fuel in aviation. Several companies and government agencies are investing in the development of hydrogen-related technologies, including hydrogen storage systems, hydrogen combustion engines and hydrogen-powered aircraft.

As in the case of maritime transport, hydrogen could also be necessary for the manufacture of fuels for use in air transport.

#### *2.6.2.5 Other Applications*

In addition to the more well-known applications, hydrogen also has other minor transport and mobility applications that might be interesting to mention.

One of the most interesting applications in the field of hydrogen vehicles are mechanical bulls or forklift. These trucks, intensive but relatively low consumption, were among the first fuel cell vehicles to be developed, and are, today, in a state of maturity that places them at a completely commercial and deployment level that reaches more than 12,000 operating units, both in Europe and in the US.

The use of hydrogen in portable fuel cells for mobile devices such as smartphones and laptops is also being explored. This could provide a clean and durable power source for these devices, rather than having to charge them with electricity from the grid.

### **2.6.3 Heat generation in buildings**

Hydrogen could be used as a fuel for heating industrial applications or buildings. In these cases, H<sub>2</sub> could be used for generating electricity and heat using the technology combined heat and power (CHP). If such plants are used in the domestic heating sector, they are also described as micro-CHP or mini-CHP plants because of their smaller outputs.



### 2.6.3.1 Buildings applications

The initial introduction of green H<sub>2</sub> as a fuel in the building sector is being by means the blended with natural gas using current operating natural gas networks and infrastructures. There are some pilot initiatives that are using 100% green H<sub>2</sub> in buildings but it is necessary to develop research and demonstration projects to know what it is necessary to adapt the current natural gas boilers and infrastructures.

In the building sector CHP plants can be operated with two strategies: The plant covers either most of the electricity or of the heat demand. If electricity prices are high, an electricity-led mode of operation is appropriate. In this way, the purchase of electricity from the grid can be minimized, or the generated CHP electricity can be fed into the electricity grid and reimbursed.

The heat produced as a by-product of combined heat and power is used to cover part of the buildings heat demand. The mostly electricity-led mode of operation results in a low thermal output from fuel cell heating systems. The remaining heat requirement of the building is covered by an additional heating system, e.g. a condensing boiler. For that reason, fuel cells are particularly suitable for buildings with a low space heating requirement, such as low-energy or nearly zero-energy buildings. In buildings with a higher space heating requirement, hybrid fuel cell heating systems, comprising a fuel cell and a condensing boiler to cover peak heating requirements, are used.

Stationary fuel cells in the output range up to 10 kW<sub>e</sub> are usually PEM or SO fuel cells. The typical CHP output range for houses and apartment buildings is 0.7 to 5 kW<sub>e</sub>. If fuel cell systems are operated with natural gas as the fuel, an existing natural gas infrastructure can be used. However, the fuel must be reformed first. In the case of PEM fuel cells, reforming takes place externally. Owing to the higher temperatures, internal reforming is possible in SO fuel cells.

Probably the biggest advantage of fuel cells over thermal power processes is the direct electrochemical conversion during electricity and heat generation and the associated higher electrical efficiency. In combined mode, i.e. electrical and thermal, fuel cells can achieve efficiencies of up to 95%. The electrical efficiency is up to 45 %. Furthermore, fuel cell systems are characterized by high efficiencies over all load points, they are quiet, have low maintenance costs and operate (locally) emission-free.

### 2.6.3.2 Industrial applications

Hydrogen is used in various industrial applications such as steel industry (primarily in metal alloying), flat glass production (hydrogen used as an inerting or protective gas), the electronics industry (used as a protective and carrier gas, in deposition processes, for cleaning, in etching, in reduction processes, etc.), and applications in electricity generation, for example for generator cooling or for corrosion prevention in power plants.

About 10% of greenhouse gas emissions come from the production of heat for industrial processes. For this reason, achieving the emission limits of the Paris Agreement will require decarbonisation of the sector that has so far received much less attention than transport or electricity production. The industrial sector has different options to decarbonize low and medium quality heat, such as heat pumps or electrical resistors, although there are fewer options in the high temperature range ( $>400\text{ }^{\circ}\text{C}$ ), where applications are more specific, as induction or electric arc furnaces in the metallurgical sector. As hydrogen can be burned or used in fuel cells, it is an emission-free alternative heat source.

Fossil fuels are the primary source of high temperature applications, although biomass and waste have been introduced as a heat source in some sectors, as well as electricity used in electrical resistors or electromagnetic technologies (infrared, microwave). However, some large-scale processes, such as reformers or high temperature furnaces, remain difficult to electrify. Any viable option to replace industrial heat sources must be able to achieve the temperatures, flows and reliability necessary for robust and continuous operation.

Hydrogen can be burned to produce high quality heat without  $\text{CO}_2$  emissions. In the presence of air, combustion reaches a flame temperature of  $2,100^{\circ}\text{C}$ , amounting to  $2,800^{\circ}\text{C}$  with pure oxygen. However, the combustion reaction is very fast and parameters must be adjusted.

Although there are currently few applications that use pure hydrogen as an industrial heat source, there are already applications where hydrogen is burned together with natural gas in boilers, stoves and engines. Hydrogen combustion systems require special burners, as well as a change of materials to prevent corrosion and brittleness of metals.



On the other hand, the technology is similar to burning natural gas, so hydrogen is a viable substitute for other gaseous fuels.

## **2.7 The costs of Hydrogen production by electrolysis**

Including hydrogen technologies in the development policy of the European Union is the strategic challenge and requires an approach based on the entire supply chain. The pursuit of hydrogen production using renewable or low-emission energy sources, the development of infrastructure for delivering hydrogen to end users and the creation of market demand must be developed simultaneously. The main target is the reduction of cost of the hydrogen production and distribution by providing the input of energy from renewable energy sources (solar, wind) at a price that ensures market competitiveness. The hydrogen cost is crucial for the development of the hydrogen economy, covering the entire chain of the technologies of hydrogen production, storage, distribution and use. The hydrogen economy includes:

- the centralized and distributed systems for the production,
- storage and transport of hydrogen using the transmission and distribution network as well as other forms of transport,
- use of H<sub>2</sub> as the end product in the transport sector, and
- use of H<sub>2</sub> for energy storage, and the production of synthetic fuels.

Nowadays, hydrogen is only a small part of the global and EU energy mix. It is still mainly produced from fossil fuels. The main hydrogen production technologies are based on the steam reforming of natural gas and coal gasification. These hydrogen production technologies are related to annual carbon dioxide emissions in the EU between 70-100 million Mg. The main target of the EU is the production of hydrogen in a carbon neutral way which could be achieved by wider use of the technologies based on the water electrolysis to make the hydrogen production fully emission-free.

The green hydrogen may be produced in the process of water electrolysis, in which electricity for the electrolysis process come from the renewable sources (photovoltaic, wind power plants). During green hydrogen production, the carbon dioxide emission is

below 1 kg CO<sub>2</sub> eq/kg H<sub>2</sub>, and the purity of hydrogen is very high (at least 99.999%, so-called hydrogen 5.0).

In the European Union there are about 300 electrolysis units which of the total production capacity of only less than 4% of total EU hydrogen production. Hydrogen seems to be an effective energy story item. The key challenge in the production of cheap hydrogen is the access to cheap electricity of EUR 10-20/MWh to make hydrogen production from electrolysis competitive. The key element of the economic assessment of green hydrogen production is the cost of the electricity which is applied in the electrolysis unit. Moreover, additional elements which influence the final hydrogen production cost are the installation equipment which is used to build the green energy source as well as the land cost and the lifetime of the installation. The electricity cost depends on several factors, i.e. the renewable energy source, the location and land cost, the design, and the sizing of green energy source. (Benghamen et al.) presents the cost range of hydrogen using different green energy sources (see Fig. 2-3).

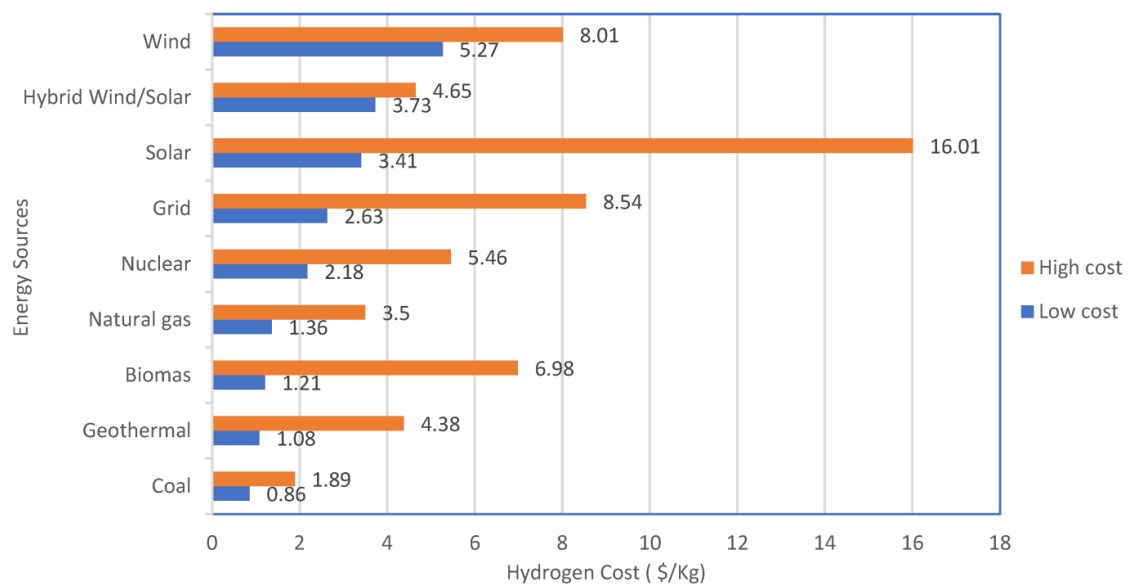


Figure 2-3. Hydrogen production costs for different energy sources

Kayfeci et al. presented the comparison of hydrogen production costs related to various production methods (see Fig. 2-4).

Of course, the cost of hydrogen production depends also on the weather conditions which significantly influence the electricity production with the application of the PV and wind power plants technologies. The relationship between the hydrogen production costs and the type of the electrolysis unit used for the same green energy sources are presented in bibliography indicated. It could be summarized that the hydrogen cost produced by the wind/H<sub>2</sub> system coupled with the PEM varies from 5 to 9.37 USD/kg. For the AWE coupled with the wind/H<sub>2</sub> system, the hydrogen production cost is between 7.47 and 7.6 USD/kg, whereas the SOE connected with the wind/H<sub>2</sub> system gives the hydrogen production cost from 6 to 9.2 USD/kg.

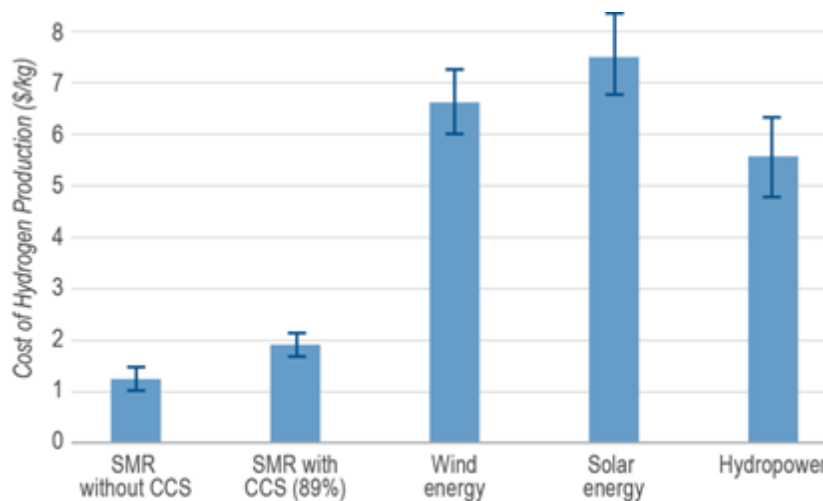


Figure 2-4. Comparison of hydrogen production costs vs various production methods.

Benghamen et al. also compared the hydrogen production costs versus electricity costs using different types of electrolysis units (see Fig. 2-5).

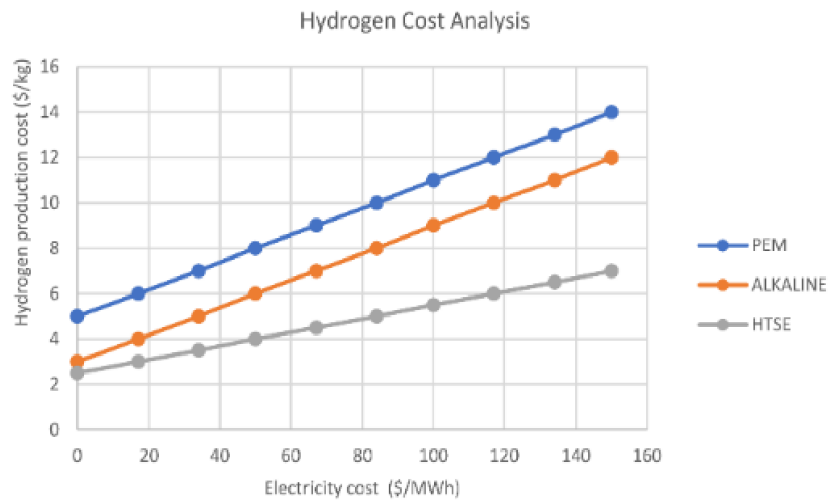


Figure 2-5. Hydrogen costs as a function of electricity costs for different types of electrolysis units used in renewable energy source/ $H_2$  systems.

### 3 Features of the implementation of green hydrogen technology in a mining area.

As for the energy and industrial transition, the coal mining regions have undergone a significant change in recent years. The European Union has set ambitious targets for reducing greenhouse gas emissions, which has led to a change in energy policy in coal mining areas. Regions have been closing their coal mines and thermal coal power stations and has opted for the diversification of the economy, promoting other economical sectors.

However, this transition has had deep social implications. Mine and coal power stations closures have led to job losses, and many workers and communities have been affected. In addition, the energy transition has resulted in the energy impoverishment of mining regions, which have moved from being an energy-producing centre to being more dependent on energy imports.

In social terms, the transition has also been a major change. Regions must evolve from a mining hub to a more diverse region in terms of its economy and society. However, this has led to social tensions.

Within the various projects carried out for the reindustrialization and enhancement of mining areas, several are included that promote the reuse and use of mining wells closed and former thermal coal power stations.

If we focus on the closed coal mines, they have characteristics that can be very advantageous for the implementation of new emerging technologies that can relate renewable energy, hydrogen and energy use.

The establishment of a renewable hydrogen production plant fulfils the above-mentioned requirements and in turn promotes the social development of a region by creating jobs related to a novel activity.

As it has been showed in the previous sections, hydrogen can be obtained from multiple raw materials, following a variety of process technologies (chemical, electrolytic, biological, photolytic, thermochemical), in which various primary energy sources can be used. Each technology is at a stage of development and each offers unique

opportunities, benefits and challenges. If we focus in the hydrogen produced by electrolysis, it is clear that is only necessary two inputs: water and electricity.

In the case of underground coal mines, it is usual the availability of large quantities of water that must be pumped and poured into natural channels. This water can be used as the main raw material for the generation of hydrogen by the electrolysis process by applying electricity.

Related to electricity, the access of the coal mines to the grid facilitates the connection of the electrolyzer to be supplied by electricity. Furthermore, in the surrounding of the mines it is usual the availability of large areas, like tips, which could be used as sites for obtaining green electricity both by wind by installing wind turbines as by solar via the installation of photovoltaic panels.

These current conditions, together with industrial infrastructures capable of utilisation and development, are shown as strengths and opportunities for the development of a new industry based on the generation of energy through renewable sources.

The more specific aspects of each of these applicable technologies, corresponding to the development of wind energy and the use of photovoltaic energy will be more widely developed in the D2.2 deliverables. and D2.3.

In this way it is possible to generate the so-called green hydrogen (clean hydrogen) whose utility can be applied in almost all sectors that today depend on fossil fuels and are difficult to decarbonize.

In addition to the environmental benefits of establishing a renewable energy source, especially in regions of energy poverty, account must be taken of the social and economic benefits it would bring the investment in new producing plants to the people of those areas.

The creation of a hydrogen generation plant, a photovoltaic plant or a wind farm can have a positive impact on job creation (greenjobs) where it is located. In a first step, during its construction and commissioning as well as for its conservation, production and maintenance, as well as in the supply chain to transport and store the energy produced.



Job creation in these facilities is not the only way they can have a positive impact on the local economy. They can also attract other companies that want to establish themselves in the region to take advantage of renewable energy or offtakers for the use of green hydrogen.

For the design and implementation of an installation such as the one proposed, a number of preliminary factors identified in the following section should be considered.

### **3.1.1 Previous considerations**

The implementation of any process or installation must first consider several factors during its project phase since its economic, political, environmental, socio-cultural and legal environment (PESTEL analysis), in addition to those that directly affect the proper functioning of the activity such as logistics, supply of raw materials, suppliers and customers.

One of the main objectives is to take advantage of the resources found in the particular regions and mining areas covered by this project. The closed mining wells are presented as a source of supply of the main raw material such as water while providing a solution to a problem of management of discharges to current channel.

There are two important parameters to consider regarding the use of this well water for the heating of a hydrogen generation plant, such as quality and quantity.

The amount of water or water flow to be delivered as an input for plant extraction must be realised by pumping. The existing facilities already have the equipment and facilities to implement this pumping so these are feasible. Obviously, the flows required by the electrolyzers will not be the same as those currently pumped, necessitating the inclusion in the design of a suitably sized intermediate reservoir, the main function of which will be to provide the supply for the proper operation of the electrolyzers in terms of the volume and flow required.

Regarding water quality, electrolyzers need a very good quality of purified water especially talking about mineralogical concentration, turbidity or electrical conductivity to optimize their production and performance as well as to extend their useful life, thus

reducing their maintenance by avoiding additional economic costs and not reducing productivity.

The quality of the water currently pumped from the closed mining wells is continuously monitored by means of periodic checks and analyses and its physico-chemical characteristics are well known. As they are subsoil waters, these characteristics vary in each location and depend mainly on the mineralogical formation of the area in which we are.

In order to adapt these waters to the requirements that the manufacturers of electrolyzers request for their proper functioning, it is necessary to have a treatment plant located between the pumping well and its entrance to the plant.

The most widely used technology for these applications and similar facilities is based on ion exchange-based processes for the replacement of calcium and magnesium cations with sodium and later osmosis for the removal of minerals and turbidity independent that it needs some additional process depending on the particular characteristics.

Given these conditions, the production of hydrogen in quantity and expected high quality can be considered.

In addition to the previously considered, the waters of the mine well present another peculiarity that can be an opportunity that must be considered and appropriated.

Geothermal energy is a form of renewable energy that harnesses the natural heat of the Earth's interior. In this case, water in a mining well could be used as a heat source to produce thermal energy. To do this, hot water is extracted from the well and passed through a heat exchanger, where heat is transferred to the domestic heating system. The water is then cooled and returned to the well. This system implies a reduction in CO<sub>2</sub> emissions and other polluting gases.

This use has already been tested and put into use previously with highly positive and promising results in some mining areas such as Barredo mining well and Fondon mining well, both in Asturias and in Heerlen (Netherlands).

Furthermore, the heat produced in the electrolysis process can be transmitted to geothermal system and improve the field of this.



Other issue that must be taking into consideration is that producing green hydrogen requires renewable energy, such as solar or wind, which is used to electrify hydrogen production from water. That is why the search for suitable areas or surfaces for the placement of solar panels or windmills has become a key issue for the development of this technology.

The closure of mining wells has left large areas of tailings in mining regions which, in many cases, can have a negative impact on the environment. However, these areas can be an opportunity to be reused for the installation of solar panels and wind farms, which would allow to take advantage of these areas for the generation of clean and sustainable energy. Both options are deployed in the deliverables D2.2 and D2.3 of this project.

In addition, the use of these areas avoids the use of other potentially usable areas which may have other advantages or disadvantages, especially from a social point of view.

As indicated in previous points, one of the most important factors within the project is the choice of electrolyser technology to be applied. Currently there are 3 main types of electrolyzers of water that can be decided: Alkaline water electrolysis (AWE), proton exchange membrane (PEM) and solid oxide electrolysis (SOEC).

Table 3-1 shows a comparison between the most relevant characteristics of the three main types of water electrolysis.

Hydrogen production has been identified as a key technology to reduce carbon emissions and transition towards a more sustainable energy system. However, to achieve widespread adoption of hydrogen as an energy carrier, it is important to identify potential offtakers that can use the hydrogen for their energy needs.

As it has been mentioned above, there are several potential offtakers of hydrogen production, including industries that currently rely on fossil fuels for their energy needs. For example, the transportation sector could potentially use hydrogen to power fuel cell electric vehicles, which offer the advantage of zero emissions and long driving ranges. In addition, hydrogen can also be used in the manufacturing sector to produce ammonia for fertilizers, as well as in refineries to remove sulfur from crude oil.

Table 3-1. Comparison between the three main water electrolysis technologies. Own processing

Parameter/Technology	PEMWE	SOWE	AWE
Operating temperature (°C)	50-80	500-1000	60-90
Maximum operating pressure (bar)	4-80	15	1-60
Current density (A/cm <sup>2</sup> )	<1-10	0,3-2	0,2-0,6
Potential of the cell (V)	1.8-2.2	0.7-1.5	1.8-2.4
Electrical efficiency (%)	46-69	74-81	51-71
Degradation (μV/hour)	4-8	n.a.	1-3
Degradación of efficiency (%/year)	0.5–2.5	3–50	0.25–1.5
Useful life (hours)	30,000-100,000	8,000-30,000	60,000-120,000
Cold start time (min)	<20	>60	20-120
Hot start time (s)	<10	900	60-300
Load range (%nominal)	0-160	(-100) 20-100	10-110
Hydrogen purity (%)	99.99-99.9999	99.9	>99.5
Hydrogen production (Nm <sup>3</sup> /hour)	1-400	<40	5-1.400
Specific consumption (kWh/Nm <sup>3</sup> )	4.4-6.5	3.2	3.8-5.9
Nominal stacking power (kW)	10-2,000	2.2	30-6,000
CAPEX (€/kW)	1,700-2,500	>2,000	2,500-5,000 / 800-1,700
OPEX (%CAPEX/year)	3-5	n.a.	2-3

Another potential offtaker of hydrogen production is the power generation sector. Hydrogen can be used in gas turbines to generate electricity, or in fuel cells to produce electricity and heat. This can be particularly useful in areas with high renewable energy penetration, where hydrogen can be produced using excess renewable energy and stored for use during periods of low renewable energy availability.

Finally, the residential and commercial sectors could also be potential offtakers of hydrogen production. Hydrogen can be used in fuel cells to generate electricity and heat for buildings, which can provide a clean and efficient alternative to traditional heating and electricity generation methods.

Other important issue is the permitting process. The installation of a chemical hydrogen production plant would be subject to various administrative and legal procedures to ensure compliance with environmental and safety requirements.

First, it would be necessary to obtain a series of permits and authorizations for the construction of the plant by the municipality. This would include obtaining a building license and activity permit, as well as submitting a detailed technical project that complies with applicable rules and regulations. In addition, authorizations would be required from different administrations and agencies, such as the Cantabrian Hydrographic Confederation, the Ministry of the Environment or the Ministry of Industry.

Secondly, an environmental impact assessment must be carried out, which is a mandatory legal procedure for certain industrial activities that may have a significant impact on the environment. The environmental impact assessment would assess the potential effects of the hydrogen production chemical plant on the environment and measures to minimise or compensate for those effects.

Third, the installation of the plant should comply with all applicable safety rules and regulations. This would include the implementation of specific safety measures, periodic inspections and audits and obtaining the necessary permits and authorisations for industrial safety.

## 4 Best Practices

### Hydrogen production plant in Pozo Fondon (Asturias)

Within the various projects carried out for the reindustrialization and enhancement of mining areas, several are included that promote the reuse and use of mining wells closed in the central areas of Asturias such as Mieres and Langreo (see Fig. 4-1 and 4-2).

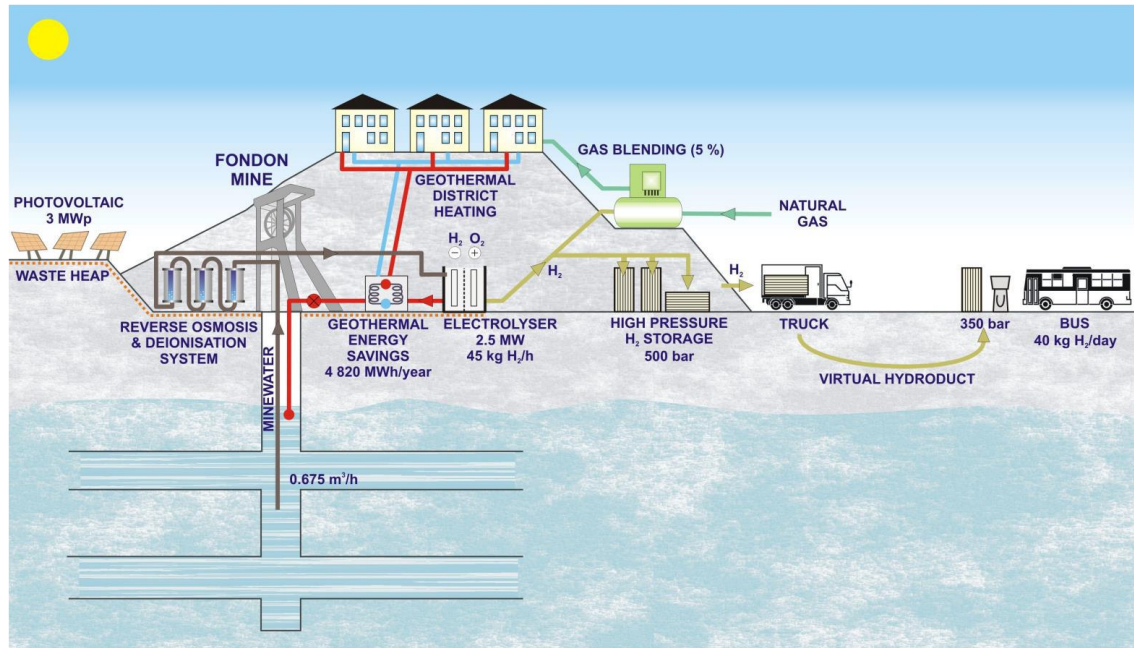


Figure 4-1. MINE-TO-H2 project graphical concept

These closed coal mines have characteristics that can be very advantageous for the implementation of new emerging technologies that can relate renewable energy and energy use.

Like other mining regions throughout the world, the mining region of northern Asturias presents, can and must face an energy transition based on clean and renewable energies for the future.



The establishment of a hydrogen production plant fulfils the above-mentioned requirements and in turn promotes the social development of the region by creating jobs related to renewable energy.



Figure 4-2. General view of Pozo Fondon and the new electrolysis plant projected.

This area has many mining wells that can be perfect locations for the implementation of this type of project or even where replicas of the initial can occur. It has been decided to start with the so-called Pozo Soton as a starting location for this project to adjust to the required characteristics as shown in Figure 4-3.

The project is promoted by a consortium of leading companies in their respective sectors as HUNOSA, DURO FELGUERA, NORTEGAS, UNIOVI and GIG and covering all aspects and functions of the project to develop each of the steps (engineering, production, transport and end use).

Among the main interesting aspects of this project, we can highlight the combination of the reuse of the facilities of a closed mining pit, the use of renewable sources for energy generation, the production of hydrogen as an energy vector, geothermal energy, the reduction of CO<sub>2</sub> emissions in land transport, the generation of new jobs and the promotion of the energy transition. The main features are described below.

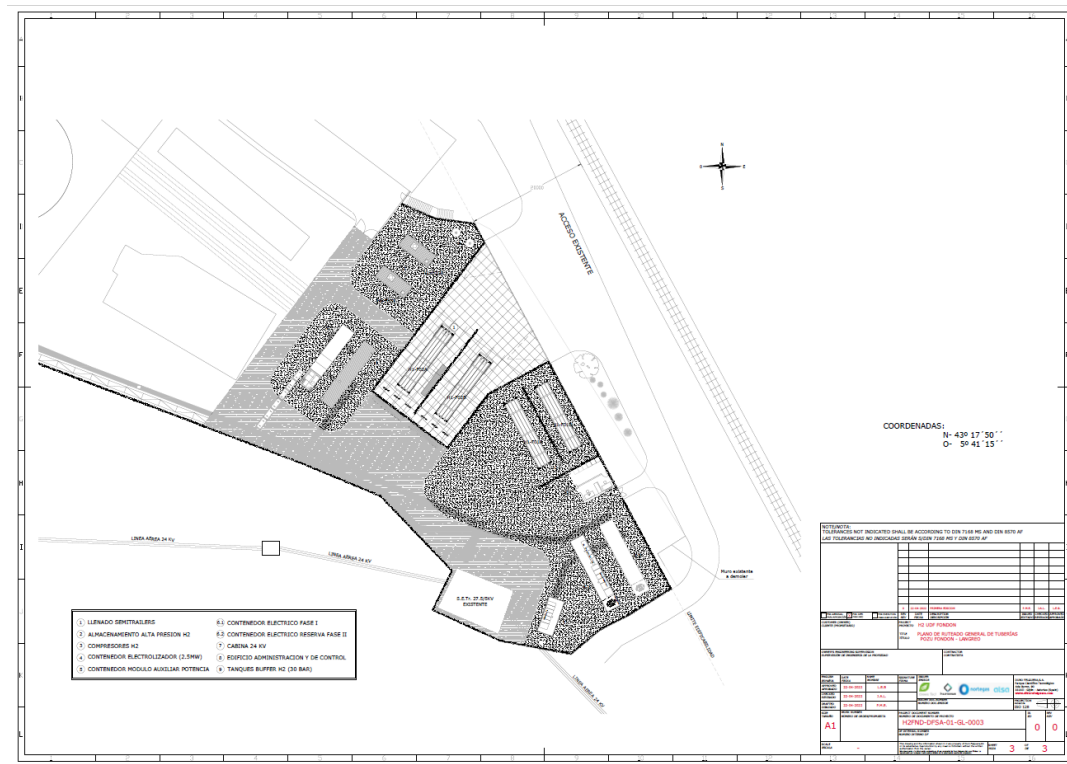


Figure 4-3. Hydrogen plant projected in Pozo Soton.

The projected power of the electrolyzer will be 5MW<sub>e</sub> so the pumped water flow of the mining well will be sufficient for its feeding and continuous production.

The technology selected for hydrogen production is the electrolysis of water from the mine well and although it has not yet been definitively defined, the electrolyzers that are shown to be most advantageous are of the PEM type.



The annual hydrogen production is estimated at 540 Mg per year and to achieve this goal, the operation of these electrolyzers would take 12,000 hours per year to obtain high quality hydrogen with a purity of 99.998%.

In accordance with this production data, and according to the manufacturer's specifications, 8.9 litres of purified water must be supplied to the electrolyzers per kg of H<sub>2</sub> produced.

The characteristics of the groundwaters of Pozo Soton are sufficiently known by HUNOSA through periodic and continuous controls in such a way that they do not present physico-chemical problems for their application. In this respect, the addition of additional products is not considered necessary to avoid problems of corrosion or embedding in the pipes of the installations. Even so, an osmosis and desionisation treatment plant is necessary to consider it for optimizing the performance of electrolyzers as well as reducing their maintenance. This process needs up to 15 Mg of water - not counting losses - to produce one tonne of hydrogen. Water treatment systems typically need about two Mg of impure water to produce one tonne of purified water. In other words, one tonne of hydrogen needs not nine, as usually stated, but 18 Mg of water. If losses are considered, the ratio is close to 20 Mg of water for every tonne of green hydrogen. That means than 8,100 m<sup>3</sup>/year of raw water need to be pumped from the mining well.

The water coming from the mine has another characteristic that aims to be exploited within the same project and is that the temperature with which it proceeds can be used as geothermal for domestic use for heating and hot water through the intermediate use of a heat exchanger.

This use of mine water is not new and is already replicating successfully at other points such as the Barredo well in Mieres.

Both uses of the well water are perfectly compatible since while the water intended for geothermal is pumped directly from the well, water for the production of hydrogen is pumped from the nearby nozzle so it is two independent pumping points.

The hydrogen generation plant must be powered by electricity for the production of hydrogen by electrolysis. The objective of this project is that this electricity is produced

by renewable energies (wind or solar) for the final production of green hydrogen. Pozo fondon has a location in which it is feasible to place both systems of renewable sources, which opens the possibility of studying both technologies for their implementation.

This project aims to take advantage of the large areas of the tailings created by the waste from the mining wells as a perfect location for the placement of solar plants for the generation of electricity necessary for the production of hydrogen.

The proximity and size of these dumps is considered sufficient to house a photovoltaic plant for the production of at least 6 MW<sub>e</sub> needed without additional work of settlement and soil consistency.

The estimated electricity consumption is 44 kWh per kilogram of hydrogen produced by the designed plant which is in line with the production of the photovoltaic plant.

After production, the final hydrogen obtained will be intended for two main uses. The first is the injection into the natural gas network for its mixture and the second is the use as fuel for mobility.

Previous the final use, the stored of H<sub>2</sub> in specific deposits is needed. The project considers 4 cilinder racks of 1,073 kg H<sub>2</sub> each and 500 bar of pressure.

The production and obtaining of oxygen as a byproduct of the process of electrolysis of water, should be considered as an economic aid for the viability of the project since it is a product with current demand and therefore can be commercialized.

From the point of view of economic balance and thus be able to evaluate its viability, the project requires an initial investment of 11,2 M€ distributed for the photovoltaic plant, grid connection and production.

The estimated useful life for these facilities is approximately 20 years, and the final result may vary depending on considering 2 different action scenarios depending on the time and that may condition the viability of the project.

The first is that the electricity production by the photovoltaic plant is higher than that consumed by the electrolysis and therefore that surplus can be sold.

In the second case, the photovoltaic plant does not produce enough electricity to supply the production of hydrogen and therefore the supply of electricity from the grid is needed.

In any of the scenarios considered, it is now known that the production price of green hydrogen is still higher than the price of fossil fuels or gray hydrogen, which makes the presence of subsidies by governments necessary to promote the viability of this type of industries. The trend is favourable and this production price is increasingly low due to the development of technology and is expected to be self-sufficient in the coming years.

Another impediment that must be overcome for the establishment of this type of industry are the authorizations by the different administrations involved in the granting of such authorizations (municipalities, environmental administration, governments, ...) as the steps, deadlines and difficulties encountered may call into question the implementation of the programme.

Finally, benefits from the social and environmental point of view must be considered as a plus. The final goal of this project is the creation of jobs related with green energy. In this way, the estimation of new jobs is about 26 during construction of new installations and 12 positions for the continuous operation, production process and maintenance.

The environmental benefit has also been estimated due to the presence of electricity generation from renewable sources and the replacement of fossil fuels with green hydrogen, which reduces CO<sub>2</sub> emissions to the atmosphere by approximately 4,520 Mg of CO<sub>2</sub> per year.

## 5 Demosite Installation. Main Economic & Technical characteristic

The aim of this chapter is to simulate a project of installation of a plant producing green hydrogen by electrolysis in a mining area and thus to have a general idea about the initial technical and economic aspects.

It is indicated the installation of a plant for the production of hydrogen by means of water electrolysis by means of electricity produced in a photovoltaic plant where the most advisable technology would be by means of PEM electrolyzers, thus producing green hydrogen and thus contributing to the decarbonisation of the electricity sector in energy-poor and transition mining regions.

The use of PEM technology water electrolyzers could be chosen against alkaline water electrolyzers (although the latter are a more mature technology) for three main reasons:

- The hydrogen produced is of such high purity that it can be used directly in the most demanding applications, as a fuel in PEM technology fuel cells.
- The dynamic response of this type of electrolyser is much faster than that of AWE electrolyzers, especially with regard to cold start time, which is vital if photovoltaic and hydrogen production are to be synchronised or if grid fluctuations are to be absorbed.
- The working load range covers almost all scenarios, from an operation to almost zero production to overloads of more than half of its rated power.

In particular, an installed electrolysis power of 5MW<sub>e</sub>. In order to keep the electrolysis plant in operation and the hydrogen generated can be considered as renewable, it must have an installed photovoltaic power of at least 10MW<sub>p</sub>. The efficiency of the electrolyzers is estimated at 75 MW<sub>e</sub>/Mg H<sub>2</sub>, the operating hours of the electrolysis process being 6,000 h/year.

The annual production of hydrogen from the plant is expected to be 540 Mg per year, with a storage in 4 cylindrical racks of 1,073 kg of hydrogen per unit at 500 bar of pressure.

Additionally, the plant will also produce oxygen with an expected yearly production of 4,320 Mg. The purity of the hydrogen produced will be higher than 99.999%.



To ensure that the plant operates efficiently, a water purification system is in place to provide purified water for the electrolysis process. The water consumption of the plant is also optimized to 23,700 m<sup>3</sup> per year (15 l/kg H<sub>2</sub>).

Regarding the necessary investment, several scenarios have been considered. The initial investment could be about 10M€ (photovoltaic plant is also included). Initially, it is planned to fix a capital of 40% of this investment, looking for soft financing of outstanding amounts as a first option. Anyway, in case of difficulties to obtain this financing, all the investment will be covered as 100% Capital directly between the partners against their balance (Direct Investment).

In case of an underground coal mines there is little available data on pilot or demonstration projects. In this exercise we have used data and information provided by a consortium of leading regional companies.

Mine water represents an essential raw material for producing green hydrogen by electrolysis. This process needs up to 18 Mg of water - not counting losses - to produce one tonne of hydrogen. Water treatment systems typically need about two Mg of impure water to produce one tonne of purified water.

In other words, one tonne of hydrogen needs not nine, as usually stated, but 18 Mg of water. If losses are considered, the ratio is nearly 20 Mg of water for every tonne of green hydrogen.

The Green hydrogen plant could be designed with a 5 MWe of electrical power dedicated to hydrogen generation; the electrolyser will allow a nominal flow rate of 500 Nm<sup>3</sup> H<sub>2</sub>/h (0.012 kg H<sub>2</sub>/s = 1078 kg H<sub>2</sub>/day). The purity of the H<sub>2</sub> generated will be 99.998%, and the operating range is between 5 and 125% of the nominal H<sub>2</sub> flow rate.

The hydrogen produced will be sold to power electro-intensive industries or companies nearby.

Table 5-1 presents the theoretical Green hydrogen plant parameters.

Table 5-1. Green hydrogen plant deployment parameters

Parameter	Value
Installed capacity	5 MWe
Estimated investment (plant life: 15 years)	10 M€
Functioning hours of the installation for one year	6,000 h
Annual hydrogen production	540,000 kg
Operating expenses (personnel, maintenance, repairs)	250,000 €
Electrical consumption of the plant	10 MWh
Hydrogen sale price	7 €/kg
Electricity cost (from Virtual Power Plant)	55 €/MWh

Table 5- presents the cash flows for the first three years, using constant 2022 euros, annual depreciation of 6.7% and working capital of about 9% of operating revenues.

Table 5-2. Cash flows calculation for Green hydrogen plant (k€)

Item	2022	2023	2024
Capital expenditure	(10,000)		
Working capital	(170)		
Operating revenues		1,890	1,890
Operating expenses		(1,240)	(1,240)
Depreciation (15 years)		(333)	(333)
EARNINGS BEFORE INTEREST AND TAXES		317	317
Taxes (25%)		(79)	(79)
NET INCOME		238	238
CASH FLOW (Net income + Depreciation)	(10,170)	571	571

Finally, considering an 8% capital cost, the expected financial outcomes for 15 years will be as Net Present Value (NPV):

$$NPV = -10,170 + \frac{571}{(1 + 0,08)} + \frac{571}{(1 + 0,08)^2} + \dots + \frac{571}{(1 + 0,08)^{15}} = -283k\text{€}$$

$$\text{Internal rate of return (IRR)} = 7 \%$$

Thus, the investment is not feasible unless a specific subvention is obtained for developing the Green hydrogen plant. This is why we will suppose that receiving a 50% subvention of the total investment is possible, which aligns with Big Ticket projects within the Research Fund for Coal and Steel (RFCS). So, taking into account a subvention of 2.5 M€, the new expected financial outcomes will be:

$$NPV = -7,670 + \frac{571}{(1 + 0,08)} + \frac{571}{(1 + 0,08)^2} + \dots + \frac{571}{(1 + 0,08)^{15}} = 2,217k\text{€}$$

$$\text{Internal rate of return (IRR)} = 20 \%$$

$$\text{Payback Period (PP)} = 7 \text{ years}$$

The useful life of the installation can be estimated at about 20 years according to manufacturer recommendations which would provide during this period a reduction of CO<sub>2</sub> emissions by 4,520 Mg per year.

This initiative, in addition to the initial investment it represents, would contribute to the development of the entire value chain through the revitalization of local suppliers and creating skilled jobs both in the construction phase and in the operational phase of the project.

An estimate of the jobs that could be generated indicates that 130 jobs could be created during the construction phase, while 5 skilled jobs would be needed during the plant's life. This social impact would help the development and growth of the area.

## 6 Conclusions and lessons learnt

The present report shows a promising combination of different and novel technologies that can be used as a bridge and transformation between an industrial network exhausted from the past such as coal mining wells and the development of renewable energy sources that are the energy future.

The following important implications and conclusions emerged from the assessments:

1. The closed coal mines are currently under-used as remnants of a large industry of the past and may present great opportunities for their use as a source and supply of water as the main raw material for hydrogen production by building a plant based on electrolysis technology.
2. The choice of the applicable technology for the production of hydrogen allows the possibility of generating so-called green hydrogen because the contribution of electricity would be generated by renewable energies. This project includes the possibility of building a photovoltaic plant or wind farm for such production due to the extent of land available in these mining areas.
3. It should be remembered that production of hydrogen via electrolysis is expensive. Economic assessment developed for the purpose of this study showed that the investment is not feasible unless a specific subvention is obtained for developing the Green hydrogen plant. This aligns with the 50% subvention given by the Big Ticket call for proposals within the Research Fund for Coal and Steel (RFCS).
4. Although it is currently in a very incipient phase, the rapid development of the technology of the green H<sub>2</sub> will allow its jump to the commercial phase in a short space of time. This combination of processes brings environmental benefits of great importance for the area both by the absence of pollution and by the reduction of emissions of Mg of CO<sub>2</sub> expected.
5. In this report has also been shown in order to advance the ecological transition to a neutral economy in greenhouse gas emissions has developed a hydrogen production plant and thus contribute to the decarbonisation of the electricity



and mining areas in a state of energy poverty. The final product generated can be injected into the existing natural gas network, transported as or used as fuel such as vehicles.

## 7 Glossary

AFC – Alkaline fuel cells

AWE – Alkaline water electrolysis

CAPEX – Capital expenditure

CHP – Combined heat and power

COP – Coefficient of performance

DMT-THGA – DMT-Gesellschaft für Lehre und Bildung mbH

DRI – Direct iron reduction

FA – Formic acid

FAEN – Fundación Asturiana de la Energía

GDL – Gas diffusion layer

GIG – Główny Instytut Górnictwa

HUNOSA – Hulleras del Norte, S.A.

ICP-AES – Inductively coupled plasma-atomic emission spectrometry

ICP-OES - Inductively coupled plasma-optical emission spectrometry

IRR – Internal rate of return

LOHC – Liquid organic hydrogen carriers

MCFC – Fused carbonate fuel cells

MEA – Membrane electrode assembly

MW – Mega Watt



MWh – Mega Watt hour

M&B – Magellan & Barents

NEC – N-ethylcarbazole

NPV – Net present value

OPEX – Operational expenditure

O&M – Operation & maintenance

PAFC – Phosphoric acid fuel cells

PCI – Lower calorific value

PCS – Higher calorific value

PEM – Proton exchange membrane

PEMFC – Proton exchange membrane fuel cells

PEMWE – Proton exchange membrane water electrolysis

PP – Payback period

PV – Premogovnik Velenje d.o.o.

REA – Research Executive Agency

SOEC – solid oxide electrolysis cell

SOFC – solid oxide fuel cells

SWE – Solid water electrolysis

SWOT – Strengths, weaknesses, opportunities, and threats

TRL – Technology readiness level



UNIOVI – Universidad de Oviedo

WEGLO – Węglokoks S.A.

XRF – X-Ray Fluorescence

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