Green Hydrogen Production from Treated Wastewater

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Foreword

Australia's National Hydrogen Strategy emphasises the country's enormous potential to become a key global producer of clean hydrogen.¹ Achieving the ambitious goal of generating green hydrogen through water electrolysis at an economically viable cost of \$2 per kilogram ('H₂ under \$2') will confer the advantage of harnessing a cost-effective energy resource over fossil hydrogen.² Nevertheless, we are grounded by the present reality: the journey towards cost-effective and sustainable hydrogen remains a persistent challenge. The current capital cost of green hydrogen, evaluated at US\$4-6 per kilogram by the International Renewable Energy Agency (IRENA), underscores the complexity of this undertaking.³

Technological innovations, improved electrolyser designs, and cost reductions contribute to the growing feasibility and scalability of the green hydrogen industry. Although countries like Australia have ample renewable energy potential due to abundant sunlight and wind, there's a significant challenge in securing sufficient water for a largescale green hydrogen economy. Interestingly, many regions with high renewable energy potential face water scarcity, posing a potential hurdle to developing a green hydrogen industry. Recycled water from wastewater treatment plants boasts an abundant supply and maintains a consistent flow throughout the year. From an economic standpoint, using recycled water for hydrogen production holds the potential for cost advantages compared to desalination water (\$5 kL⁻¹) and drinking water (\$2.75 kL⁻¹), with an estimated cost of approximately \$0.70 kL^{-1.4}

Globally, there is a substantial amount of wastewater, totalling 380,000 GL per year, significantly exceeding the 34,500 GL annual requirement to produce the anticipated 2.3 Gt of hydrogen in a fully developed hydrogen economy.^{5, 6} Further, in an Australian context, 1720 GL of effluents from tertiary wastewater treatment plants are discharged back into the environment annually.⁵ If all of this treated wastewater can be efficiently converted into hydrogen, it has the potential to produce approximately 0.1 Gt of green hydrogen, reaching the projected global hydrogen demand by 2050.⁵

Accordingly, integrating water electrolysis with wastewater treatment is a potential key strategy in the value chain of scalable and sustainable hydrogen production. However, utilizing wastewater as a hydrogen production source is challenging as current water electrolysers are designed for high-purity feed water. This leaves a significant gap in our understanding of how wastewater's impurities interact with water electrolysis systems. Furthermore, cost reduction in green hydrogen production can achieved by leveraging electrolysis co-products (such as ozone, hydrogen peroxide, and oxygen) in conjunction with co-location opportunities of green hydrogen generation and wastewater treatment.

In response, the UQ Dow Centre for Sustainable Engineering Innovation at the University of Queensland and Monash University have developed preliminary guidelines and strategies in this report to integrate wastewater treatment and water electrolysis for sustainable hydrogen production from wastewater. Our aspiration is that this report will not just be a valuable roadmap for the water industry and water utilities when planning future upgrades of a co-production of hydrogen with wastewater treatment but also a reference for designing a highly durable water electrolysis system.

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Abbreviations

AEMWEs- Anion exchange membrane water electrolysers AOTs -Advanced Oxidation Technologies AWEs- Alkaline water electrolysers BOD - Biochemical Oxygen Demand **CAPEX** -Capital expenditure CO₂- Carbon dioxide COD - Chemical Oxygen Demand FO- Forward osmosis H₂- Hydrogen H₂O₂-Hydrogen peroxide HCO₃⁻-bicarbonate HER-Hydrogen evolution reaction IRENA-International Renewable Energy Agency O₂- Oxygen O₃-Ozone OER - Oxygen evolution reaction **OPEX-Operating expenditure** PEM- Proton exchange membrane PEMWEs -Proton exchange membrane water electrolysers PTFE- Polytetrafluoroethylene PTFE- Polytetrafluoroethylene RHE- Reversible hydrogen electrode **RO-** Reverse osmosis SOEC- Solid oxide electrolyser **TDS** -Total Dissolved Solids TN -Total Nitrogen TOC -Total Organic Carbon TP - Total Phosphorus. TS -Total Solids TSS -Total Suspended Solids WWTP- Wastewater treatment plant

Chapter 1. Introduction

1.1 Background and objectives

Green hydrogen, produced through water electrolysis using renewable energy, is recognized as a key player in achieving the emission reduction targets outlined in the *Paris Agreement*. Predictions indicate that green hydrogen can provide around 38,000 TWh of energy, equivalent to 24% of the global energy requirement by 2050, while reducing emissions by about a third.⁵ IRENA estimates the current capital cost of green hydrogen to be US\$4-6 per kilogram.³ The Australian goal to produce hydrogen at a cost of less than A\$2/kg resonates with the nation's determined stance to be a world-leading clean hydrogen producer, as outlined by Australia's 2019 National Hydrogen Strategy.^{1, 2}



Figure 1-1 The supply chain and key ingredients of Australia's water electrolysis-based hydrogen economy. (Source: Herbert Smith Freehills⁷)

The supply chain and key ingredients of a water electrolysis-based hydrogen economy in Australia can be illustrated in **Figure 1-1**. Generated hydrogen can be employed as a fuel for vehicles, a feedstock for industrial processes, a means of energy storage, for heating and power generation, grid services, and various other applications. Technological innovations, improved electrolyser designs, and cost reductions have contributed to this clean energy solution's growing feasibility and scalability. Water electrolysis using renewable energy, which generally splits water molecules into hydrogen and oxygen gases, is a clean and efficient method for generating green hydrogen free from associated greenhouse gas emissions. However, a critical concern arises regarding the water availability for establishing a large-scale green hydrogen economy. Notably, countries with significant renewable energy potential, like Australia, encounter this challenge more acutely because they are located in some of the world's most arid regions.⁵

Australia is grappling with the adverse impacts of climate change and fluctuating rainfall patterns. As highlighted in the State of the Climate 2022 report,⁸ since the commencement of national records in 1910, Australia's climate has experienced an average warming of $1.47 \pm$ 0.24 °C, accompanied by a simultaneous rise in sea surface temperatures averaging 1.05 °C since 1900. The report further predicts a continued decrease in cool season rainfall across various southern and eastern Australian regions, contributing to prolonged drought conditions. Australia's climate is projected to persist in its current variability state, characterized by sporadic heavy rainfall events occurring over short durations and at different timescales.⁸ Given the escalating challenge of water scarcity facing the nation, it is imperative to explore alternative water sources for hydrogen production through water electrolysis.

Water sourced from desalination plants is one viable avenue. For example, acquiring desalinated water from the established Victorian Desalination Plant (VDP) comes at an approximate cost of \$5 kL⁻¹, in contrast to the estimated \$2.75 kL⁻¹ for procuring fresh drinking water.⁴ Although the present capacity of desalination infrastructure satisfies the water demands in the short term, it necessitates the establishment of new desalination facilities in the long term for an expansive hydrogen-based economy. When encompassing factors such as material expenses, construction of core and supporting infrastructure, and the added energy consumption inherent in their operation, the total cost could surge to \$10 kL^{-1.4} Rather than investing in more desalination facilities, a more practical approach might involve promoting

wastewater reuse and adopting a circular economy model. $^{\scriptscriptstyle 5}$

Accordingly, the second approach focuses on tapping into treated wastewater from wastewater treatment plants. This water resource boasts ample supply, maintaining a consistent flow throughout the year. Wastewater treatment plants serving large urban areas and even moderately sized towns produce millions of litres of reclaimed water yearly. Despite undergoing rigorous treatment processes, this water is predominantly discharged into the environment because of a trio of barriers: political, legislative, and cost-related, collectively impeding its broader utilization across various applications.⁴ Using reclaimed water for hydrogen production could address these challenges effectively while reducing the adverse effects of wastewater treatment facilities on local ecosystems, particularly those sensitive to changes. Furthermore, from an economic standpoint, using recycled water for hydrogen production holds the potential for cost advantages compared to desalination and drinking water, with an estimated cost of approximately \$0.70 kL^{-1.4}

Globally, there is a substantial amount of wastewater, totalling 380,000 GL per year, significantly exceeding the 34,500 GL annual requirement to produce the anticipated 2.3 Gt of hydrogen in a fully developed hydrogen economy.^{5, 6} In contrast to the significant investments needed for desalinated water and the unpredictability of stormwater, the use of treated water from wastewater treatment plants has a critical role in effectively managing water resources for a responsible and sustainable hydrogen industry. This will aid in fulfilling the water requirement for water electrolysis while eliminating the competition with drinking water demand.

The UQ Dow Centre for Sustainable Engineering Innovation at the University of Queensland and Monash University have collaborated to develop guidelines for sustainable hydrogen production from treated wastewater. The structure of the quideline is illustrated in **Figure 1-2**. Various significant features associated with wastewater treatment plants, such as access to recycled water, availability of excess land, location away from densely populated areas but near markets, and the presence of renewable energy, along with co-product utilization possibilities, make it an ideal sector for coupling with green hydrogen production. The evolution of water electrolysis has led to the emergence of four main technologies, each based on different types of electrolysers, extensively discussed in Chapter 2. Chapter 3 provides in-depth insights into the wastewater treatment processes in Australia. Chapter 4 explains the water quality gaps between wastewater effluents and electrolysis requirements. Then, Chapter 5 details the possibilities of generating and utilising the coproducts of electrolysis. Recommendations for designing the water electrolysis system in the context of synergizing wastewater treatment and green hydrogen production are finally provided in **Chapter 6**, highlighting probable advancements in treatment technologies to address the quality gaps.

We believe the developed guideline will be not only a valuable roadmap for the water industry and water utilities when planning future upgrades of wastewater treatment plants but also a reference for designing highly durable water electrolysers. Hence, the specific objectives of this report are:

- To provide a comprehensive understanding of the status of wastewater treatment in Australia, including the distribution, capacities, and processes of wastewater treatment facilities, in both theoretical and practical aspects.
- To illustrate the state-of-the-art water electrolysis technologies by introducing configurations and technical specifications

of mature electrolysers, along with preceding water treatment procedures and the associated cost for hydrogen production.

- To gain an in-depth understanding of the gaps between the recycled water quality from current wastewater treatment in Australia and the water quality requirements for hydrogen production by water electrolysis.
- 4. To offer a comprehensive and informed recommendation regarding effluent from wastewater treatment plants as an alternative source for hydrogen production. Additionally, to propose suggestions for the system design of water electrolysis specifically tailored to enhance the tolerance of water impurities in the effluent.
- To provide recommendations for wastewater treatment, emphasizing advanced treatment technologies, optimizing co-product utilization, and exploring opportunities for co-locating the industries.



Figure 1-2 Structure of the guideline for green hydrogen production using wastewater from wastewater treatment plants.

1.2 Guideline values

This guideline is intended to be used by:

- 1. Decision makers and operators from the wastewater treatment industry.
- Organizations and individuals involved in the water electrolysis industry, such as government departments and agencies, electrolyser manufacturers, energy companies, and experts in the field.
- 3. Parties interested in the development of sustainable hydrogen energy.

Integrating water electrolysis with wastewater treatment is a potential key strategy in the value chain of scalable and sustainable hydrogen production. Clean and renewable hydrogen energy, as an alternative to traditional fossil fuels, is highly desirable in response to growing concerns about climate change and its impact on Australia's development and environmental sustainability. By utilizing wastewater instead of fresh water, this strategy aims to create a sustainable solution for hydrogen production without exacerbating water scarcity issues in Australia. Further, by aligning with Australia's National Hydrogen Strategy, this combination will help Australia secure a global leading position in the emerging hydrogen economy. Therefore, utilizing wastewater for green hydrogen production through water electrolysis is attractive. However, there is uncertainty within the industry regarding the ideal

timing for transitioning. As the hydrogen landscape continues to develop, the industry must address and overcome this uncertainty to fully leverage the potential of wastewater treatment plants and establish a thriving hydrogen economy with water as a critical enabler.

These guidelines will assist the Australian water industry in better planning the design and upgrade of future water treatment facilities. Regulators and operators can draw inspiration on utilizing large volumes of treated water as a sustainable resource, reducing the water footprint. The information will guide efforts to save water consumption, which is highly beneficial for regions facing critical water scarcity and quality issues. The guideline will illuminate the potential for localized hydrogen production around wastewater treatment facilities, offering advantages such as reducing transportation costs, promoting local selfsufficiency, and enabling on-site hydrogen utilization for various applications.

In terms of the co-products of hydrogen generation, such as pure oxygen, ozone, and hydrogen peroxide, all of which hold significant promise in wastewater treatment. Ozone and hydrogen peroxide exhibit exceptional utility as potent oxidizing agents in tertiary water treatment, enhancing the removal of contaminants. Simultaneously, pure oxygen can substantially bolster the efficiency of the secondary wastewater treatment process. Recognizing the potential to leverage these co-products within the treatment processes reframes what has traditionally been categorized as a 'by-product' of electrolysis. This represents a transformative opportunity to not only add value to the hydrogen production process but also partially subsidize its costs, ultimately enhancing its commercial viability.

Besides, the guideline also provides insight into government agents or companies that aim for a synergistic approach to water resource utilization. It creates a circular economy where wastewater treatment plants not only treat and discharge water but also produce valuable hydrogen, a clean energy carrier while utilizing the co-products of hydrogen generation in the treatment process. Implementing the guideline will help Australian industries build the technology competency for the emerging hydrogen economy.

Chapter 2. Water electrolysis technologies

In a water electrolysis cell, the basic setup comprises two electrodes separated by an electrolyte, the medium responsible for conveying the generated chemical charges (anions or cations) from one electrode to the other.9 Decarbonised electricity sources are the greener and more mature options for powering these cells to produce green hydrogen, which splits water into hydrogen and oxygen within an electrolyser. This process is recognized for its environmental benefits.¹⁰ Contrastingly, alternative technologies for directly splitting water, such as concentrated solar, direct solar desalination, or photocatalytic approaches, are still in the early stages of development and are considered less mature than electrolysis driven by decarbonized electricity.^{5, 11} If driven by green electricity, water electrolysis would provide hydrogen with minimal CO₂ footprint as an inexhaustible and environmentally friendly fuel source. The principle of water electrolysis is simple, yet it allows the construction of different technological variations based on various physicochemical and electrochemical aspects.

2.1 State-of-the-art electrolysers for hydrogen production

There are four primary types of electrolysers commonly utilized across distinct technologies: Alkaline water electrolyser (AWE), proton exchange membrane water electrolyser (PEMWE), solid oxide electrolyser (SOEC), and anion exchange membrane water electrolyser (AEMWE). The differences between these technologies are based on factors such as the electrodes, electrolytes, separators, working pressures, and temperatures applied. AWE and PEMWE are already commercially used, while AEMWE and SOEC are currently at a laboratory scale.⁹ Electrolyser types are mainly differentiated by their electrolyte and operating temperature, influencing the choice of materials and components.⁹ **Appendix Table 2-1**⁹ provides an overview of the general conditions and parameters for the four technologies. It's important to note that each water electrolyser technology has its strengths and weaknesses, and the hurdles in cost reduction for hydrogen production vary depending on the specific technology employed.

2.1.1 Alkaline water electrolysers

The AWE method is the most mature hydrogen production technology through electrochemical water splitting.¹² From 1789, when Troostwijk and Diemann first introduced the phenomenon, AWE evolved to become a commercially viable solution, demonstrating its efficacy up to the megawatt scale worldwide. AWE technology offers numerous benefits, primarily associated with using alkali metal hydroxide aqueous electrolyte, typically potassium hydroxide (KOH). This allows for utilising catalysts made from non-precious metals without compromising operational performance and durability. AWE cells traditionally employ electrode materials derived from nickel, cobalt, or stainless steel.¹² AWE utilizes potassium hydroxide aqueous solutions, typically ranging from 20 to 50 wt% concentrations, to facilitate ionic conductivity between the anode and cathode electrodes. To separate the evolved gases and create pathways for potassium hydroxide to enable ionic conductivity, a porous and chemically inert separator like Zirfon[™] is employed. Zirfon[™] is a composite material composed of zirconia (ZiO₂) and polysulfone.13, 14

The reduction of water in an AWE occurs at the cathode:

 $2H_2O\,+\,2e^{\scriptscriptstyle -}\rightarrow H_2\,+\,OH^{\scriptscriptstyle -}$

and the hydroxide ion oxidation occurs at the anode:

 $OH^{\scriptscriptstyle -} \rightarrow 0.5O_2 \,+\, H_2O+\, 2e^{\scriptscriptstyle -}$

Figure 2-1 is the typical internal structure of an AWE. The cells in the system can be connected in one of two ways: either in parallel, known as a monopolar assembly, or in series, known as a bipolar assembly. In the case of all anodes (respectively cathodes), they are connected in parallel, typically using copper (or aluminium) conduction bars. This setup helps reduce ohmic drop and ensures uniform current distribution for feeding and collecting. The current is collected through endplates positioned at both ends of the assembly. The cathode and anode of stack unit cells are electrically connected.¹²



Figure 2-1 Typical internal structure and mechanism of an AWE electrolyser

The current surge in interest regarding electrolysis for energy-related purposes is fostering progress, exemplified by innovations like zero-gap configuration cells.¹⁵ Standard current densities for AWEs are around 1 A cm⁻² at 1.8 V, leading to larger physical footprints than membrane-based electrolysers. A PEMWE with a capacity of 1 GW is projected to occupy an area of 8-13 hectares, while an AWE facility with a similar capacity is estimated to require a larger space, ranging from 10-17 hectares.9 The presence of liquid electrolytes and the porous separator's high permeability to gases pose challenges for operating AWE systems at very low currents. This difficulty complicates their integration with renewable energy sources and makes the direct production of compressed gas more challenging. Despite these challenges, AWE systems exhibit advantages such as a lower capital cost compared to PEMWE and robustness, with instances of operations lasting for 30-40 years.^{13, 16}

Regardless of the configuration, the primary drawback associated with AWE cells is the production of hydrogen and oxygen (O₂) bubbles at the cathode and anode, respectively.¹⁴ Firstly, bubbles in the liquid electrolyte alter its ionic conductivity, increasing the cell's ohmic drop and the operational cost of AWE. Secondly, because the separator is porous, there is a risk of intermixing between hydrogen and oxygen bubbles if mass transport is not well-balanced, posing safety concerns and affecting gas purity.¹⁷ In practical terms, AWE cells require several hours to achieve a steady state regarding electrolyte flow, temperature, and current density (because of bubble generation).¹⁸ This characteristic makes it challenging to operate AWE in transient regimes. It complicates its integration with renewable solar or wind electricity sources, although efforts are underway to explore this coupling.¹⁹ Operating under pressure is also challenging for similar reasons.¹²

2.1.2 Proton exchange membrane water electrolyser

PEMWE technology is pivotal in producing green hydrogen, functioning through an electrochemical process to split water molecules into hydrogen and oxygen gases. Its structure comprises essential components, including anode and cathode electrodes, separated by a Proton Exchange Membrane (PEM), with an electrolyte facilitating ion conduction. As an electric current passes through water, oxidation at the anode generates oxygen gas and positively charged hydrogen ions, while reduction at the cathode produces hydrogen gas. The PEM selectively allows the migration of protons from the anode to the cathode, ensuring charge balance and facilitating the production of pure hydrogen gas. PEMWEs offer advantages such as high efficiency, fast response times, and compact design, making them versatile for applications in renewable energy storage, transportation, and industrial processes aimed at decarbonization. The anode and cathode are arranged in a sandwich configuration with a proton-conducting polymer electrolyte, like Nafion®, forming what is known as the membrane-electrode assembly (MEA). The MEA is then placed in pure water, and a cell voltage is applied to initiate the release of oxygen at the anode¹² and the hydrogen evolution at the cathode.

The typical structure inside a proton exchange membrane water electrolyser (PEMWE) is depicted in **Figure 2-2.** A slender proton exchange membrane (PEM) ensures effective functioning, typically with a thickness ranging from 100 to 200 micrometres. These membranes are commonly made of perfluorosulphonic acid (PFSA), featuring a hydrophobic backbone of polytetrafluoroethylene (PTFE), a perfluoroethylene sidechain, and a hydrophilic sulphonic acid head group. This composition enhances ionic conductivity and ensures the distinct separation of generated hydrogen and oxygen gases. PFSA ionomers are

also employed within the electrodes to facilitate ionic conductivity, often utilizing highly active, acid-resistant nanoparticulate platinum group metal (PGM) electrocatalysts loaded at a magnitude of milligrams per square centimetre. Platinum and supported platinum catalysts are frequently utilized at the cathode to facilitate the hydrogen evolution reaction (HER). At the same time, iridium oxide or mixed-metal oxides are commonly employed at the anode to catalyse the oxygen evolution reaction (OER).^{20, 21} Porous transport layers (PTLs), responsible for supporting electrodes and regulating two-phase flow, typically comprise titanium for the anode and occasionally carbon for the cathode. Bipolar plates (BPPs), which separate neighbouring anodes and cathodes, are usually made of titanium. PTL and BPP components are frequently coated with a thin layer of platinum to minimize contact resistance.^{13,} 22



Figure 2-2 Typical internal structure and mechanism of a PEMWE electrolyser

PEMWEs can be considered as a technology in an intermediate stage of development. They are commonly utilized with inlet water temperatures of approximately 60 °C and exhibit typical current densities ranging from 2 to 4 A cm⁻². This operational configuration leads to satisfactory cell voltages of 1.8 V and ensures a lifespan falling within the 6 to 9-year range.²³ A typical water process flow and balance of the plant of the PEMWE stack is illustrated in Figure 2-3. Water is typically obtained from a nearby water source and undergoes a multi-step purification process, the specific details of which are often considered proprietary information held by the system manufacturer. After that, water is supplied to the stack, which undergoes electrolysis to yield oxygen and hydrogen. To maintain high stack efficiency

and temperature control, liquid flows are typically operated far above what is needed to sustain the electrochemical reaction. As the electrolyser technologies discussed in this context are exothermic, most thermal energy is dissipated through heating the water. Typically, the liquid and product gases exit the stack together and undergo a separation process. The liquid is recirculated while the gases leave the system. In PEMWE systems, it's common to introduce water only to the anode, where the electrochemical reaction consumes it. Consequently, the only water in the cathode outlet traverses the membrane due to diffusion and electro-osmotic drag. Additional drying processes are employed to attain extremely high-purity hydrogen gas (with less than five ppm of water). ^{13, 24}



Figure 2-3 Schematic of typical water process flow and balance of plant of PEMWE stack

Extensive research aims to enhance the lifespan, boost efficiency, and reduce the costs of PEMWEs, anticipating improvements in these aspects. In operational terms, PEMWEs exhibit a compact volumetric footprint, high efficiency, and the capability to generate high-purity hydrogen. Additionally, they can directly produce pressurized hydrogen and quickly adapt to changes in load, making them well-suited to address the intermittency associated with renewable power sources.^{13, 25}

It is important to note that the electrolyte undergoes no net consumption, with only water being used. Maintaining a constant ion concentration is achievable by supplying water at a rate equal to its consumption. Throughout the electrolysis process, mobile proton species are confined within the highly acidic polymer membrane.¹² Noble metal catalysts, essential at both the cathode and anode, leverage their inertness to endure such acidity. PEMWEs can operate at high current densities, ensuring high energy efficiency while still producing gases of exceptional purity. The low gas crossover rate of the polymer electrolyte membrane contributes to achieving hydrogen with a purity exceeding 99.99%, surpassing that of alkaline electrolysers.²⁶ Despite these advantages, the considerable initial capital investment poses a hurdle to further development and application. The membrane material and noble metal electrodes significantly drive the costs of PEM technology. The most effective strategy for reducing capital costs is the development of durable electrodes made from abundant earth materials and cheap proton exchange membranes.¹²

2.1.3 Solid oxide electrolysers

Solid oxide electrolysers (SOECs) operate similarly to fuel cells but in reverse, utilizing hightemperature electrolysis to split water molecules into hydrogen and oxygen gases. SOECs consist of a solid oxide electrolyte sandwiched between two porous electrodes, typically made of ceramic materials. At elevated temperatures (typically between 500°C and 1000°C), the solid oxide electrolyte becomes conductive to oxygen ions. When an electric current is applied, oxygen ions migrate through the electrolyte from the cathode to the anode, reacting with water vapour to produce oxygen gas. Simultaneously, electrons flow through an external circuit to the cathode, where they combine with hydrogen ions to form hydrogen gas. In the SOECs, water vapour undergoes reduction at the cathode as follows:

 $H_2O(g) + 2e^- \rightarrow H_2(g) + O^{2-}$

While the transferred O²⁻ is oxidized at the anode:

 $O^{2-} \rightarrow 0.5 \ O_2(g) + 2e^{-}$

The overall reaction is $H_2O \rightarrow H_2 + 0.5O_2$.

SOECs with a typical structure in Figure 2-4 offer several advantages for green hydrogen production, including high efficiency, scalability, and the ability to utilize renewable or waste heat sources. Additionally, they can operate with a wide range of feedstocks, including pure water or steam, making them versatile for various applications in transitioning to a sustainable energy future. Ionic diffusion facilitates the transport of oxide ions from the cathode to the anode through the zirconia electrolyte. Ultra-thin ceramic membranes, ranging from 30 to 150 micrometres, are employed to minimize ohmic losses. The cathode, designed for steam, usually consists of porous nickel, while the anode for air typically incorporates porous perovskite materials like lanthanum strontium manganite. Ongoing research explores various catalyst blends, including lanthanum strontium cobalt ferrite, samarium-doped ceria, and rare-earth nickelates.

In-depth modelling of SOEC has revealed that the rate-limiting step may involve the de-sorption of oxygen at the cathode surface within the triplephase boundary. This limitation can be addressed by optimizing the microstructure of the porous composite functional layer located at the interface between the cathode and electrolyte.²⁷ Even though the elevated temperature is a factor, the diffusion of multi-component gases within porous electrodes, particularly at the steam electrode, can be a limiting factor.²⁸ The advancement of SOEC technologies has been motivated by the potential to function at high current densities, such as 3.6 A cm⁻² at 1.48 V and 950 °C, along with high efficiencies. However, challenges persist in managing electrochemical degradation and ensuring adequate thermo-mechanical stability, hindering the progress toward large-scale hydrogen production.¹²



Figure 2-4 Typical internal structure and mechanism of the SOEC

2.1.4 Anion exchange membrane water electrolyser

In the case of AEMWE, an alkaline environment is employed, utilizing an anion exchange membrane (AEM) to separate the anode and cathode (Figure **2-5**).¹³ The catalyst layer relies on an anionic ionomer to provide conductivity. Typically, AEMs consist of a polymer backbone with integrated cationic groups responsible for anion conductivity and selectivity. The key performance criteria for AEMs in water electrolysis applications include hydroxide conductivity, ideally exceeding 100 mS.cm⁻¹, and water mobility, which are closely interconnected. The water content plays a crucial role in determining the AEM's conductivity, mechanical properties, and physical dimensions, making it a significant parameter in designing AEMs for water electrolysers.¹²

AEMWEs exhibit a structure akin to PEMWEs, although there is greater diversity in the current state of technology as they are in an earlier stage of development.²⁹ Sometimes, AEMWEs are supplied with a liquid electrolyte containing aqueous potassium hydroxide or aqueous potassium carbonate with a concentration below 1 M.³⁰ Consequently, the primary ionic species is hydroxide. The elevated pH level enables the utilization of various nanoparticulate transition metal-based catalysts, predominantly nickel or nickel-containing materials, at both the anode and cathode. However, ongoing research is focused on developing new catalysts, and precious metals continue to be frequently employed.^{13, 29}



Figure 2-5 Typical internal structure and mechanism of the AEMWE

AEMWEs are attracting attention due to their potential to retain operational advantages like PEMWEs, all while eliminating the need for costly and rare critical raw materials like iridium and platinum. Recent academic literature on AEMWEs indicates operation around 60 °C at 2 A cm⁻² and ~1.9 V vs. RHE.³¹ Like PEMWEs, they exhibit quick response times, generate pure hydrogen, have a compact volumetric footprint, and directly produce pressurized hydrogen. However, a current drawback lies in the relatively low rate of hydrogen evolution reactions under alkaline conditions.^{13, 32} Despite multiple publications with AEMWE performance data, studies on cell performance stability are scarce. Most stability tests at constant current density reveal a significant performance decline within 200 hours of operation.¹² The primary degradation mechanism involves hydroxide (OH⁻) attacking the polymer backbone, leading to membrane collapse and catalyst layer dissolution within a few days.⁹ Issues such as ionomer-catalyst detachment, ionomer poisoning, and catalyst degradation further compound the challenges.¹² Hence, advancements in membrane,

ionomer, and catalyst technologies are necessary to meet the extended lifetimes essential for commercial systems.¹³

In summary, most green hydrogen initiatives use PEMWEs and AWEs due to their matured technology. However, emerging technologies such as AEMWE and SOEC are gaining traction as potential candidates for large-scale hydrogen production. Water electrolysis stands out as the predominant electrochemical method for hydrogen generation, and its significance is expected to increase with the growth of renewable energy production. As the demand for sustainable hydrogen continues to rise, ongoing research and development in AEMWE and SOEC technologies are poised to contribute to diversifying green hydrogen production methods, ensuring a robust and versatile approach to meet the evolving needs of a greener and more energy-efficient future. Overall, the effectiveness of water electrolysis technologies is heavily reliant on factors like electrolytes, catalysts, separators, pressures, and temperatures. Presently, hydrogen production through electrolysis is comparatively more expensive than alternative methods. The following section will discuss the status of industrial manufacture and market.

2.2 Manufacture and cost of water electrolysers

2.2.1 Manufacture of water electrolysers The market for electrolysers used in water electrolysis has been experiencing significant growth in recent years, driven by increasing interest in renewable hydrogen production and the decarbonization of various industries, including but not limited to transportation, power generation, and industrial applications. In 2022, the worldwide production capacity for electrolysers reached nearly 11 GW annually, marking a growth of over 25% from the preceding year. It is noted that the global electrolyser market is relatively concentrated because large enterprises are currently very active in acquiring and merging small and medium-sized electrolyser companies into their subsidiary portfolios. We listed major manufacturers of electrolysers in **Appendix Table 2-2**. The major manufacturers are mainly from the United States, China, and Europe. Owing to the long history of development, the scope and market of AWE manufacturing is the largest. The situation of manufacturers may change as the market is dynamic, with acquisitions being common.

At this point, the market is still concentrated in the hands of a few players, mainly using manual assembly and relying on individual projects to adjust production. Most manufacturers are in a stalemate situation where funding and investment are needed to expand capacity, but project capacities cannot be met with such a negligible manufacturing capacity. The leading manufacturers are expanding capacity in anticipation of future growth and discovering some economies of scale. Taking a snapshot of the EU,³³ the green hydrogen strategy aims to construct a 2 x 40 GW electrolyser capacity by 2030 in the EU and 40 GW outside the EU in neighbouring countries (Figure 2-6). An additional 80 - 120 GW capacity of Renewable Energy Sources (RES) will be split into two phases.³⁴ The first phase, until 2024, targets 6 GW of electrolysers to produce up to 1 Mt of hydrogen, primarily for the chemical industry and heavy-duty transport. In the second phase, until 2030, over 40 GW of electrolysers, including decentralized hubs, are expected to be deployed, producing 10 Mt of hydrogen. This phase aims to cater to more sophisticated applications like power generation and storage and a broader refuelling station infrastructure for mobility applications. The environmental impact of electrolysis depends on the electricity supply, with 'green' hydrogen produced from renewable sources considered decarbonated. While electrolysis processes are technologically advanced, they are not yet widely deployed at an industrial scale and face cost challenges compared to traditional fossil fuel processes.



Figure 2-6. The majority of electrolysis capacity are currently operational and planned for installation. Sources: IEA; Monitor Deloitte Analysis. Figure reproduced from Reference.³³

2.2.2 Water requirements

To ensure the success of this approach in meeting hydrogen production goals, it is essential to identify the water requirement for water electrolysis and assess their compatibility with the available quantities of treated wastewater. Theoretically, 9 kg of H₂O is required to produce 1 kg of hydrogen gas. Considering the overall process, including demineralization and electrolyser cooling, this can increase to 60 - 95 kg of water per 1 kg of hydrogen.⁵ **Appendix Table 2-3**³⁵ presents hydrogen flow rates for five manufacturers with their energy and water consumption values.

2.2.3 Cost of water electrolysers

Electrolysis for green hydrogen production is technologically advanced (TRL > 7 for AWE and PEMWE) but not widely deployed at an industrial scale. In addition to regulations and market design, their costs are prohibitive compared to traditional fossil fuel processes (2 to 4 times). According to the Hydrogen Council, hydrogen could help meet almost a quarter of the global energy demand by 2050, creating a US\$ 10 trillion addressable market. However, the cost of green hydrogen (US\$3-6 kg⁻¹, based on IRENA analysis⁹) is still 2-3 times more expensive than blue hydrogen (produced from fossil fuels with carbon capture and storage) despite the falling renewable power costs. Meanwhile, Australia has launched the "H₂ under 2" target, targeting production costs below \$2 kg⁻¹ for a competitive hydrogen price across various applications. Thus, further cost reductions are critical to reaching the ultimate green destination. Over the last few years, many countries have adopted green hydrogen policies and strategies to hit the target.

Electrolyser cost plays a defining role in the overall economic viability of hydrogen electrolysis. IRENA calculates that the stack of electrolysers contributes 45% of the total system cost. The remainder comes from the balance-of-plant components: power supply (28%), water circulation (12%), hydrogen processing (11%), and cooling (4%).⁹ The cost of electrolysers will be critically important to their success and competitiveness against other routes to producing hydrogen and other low-carbon fuels. Figure 2-7 shows that current capital expenditures (CAPEX) for the electrolysers' estimates vary by magnitude from €170 to 2.300 per kW of capacity.^{9, 36-38} The actual deviation is by technology type. For example, the PEMWEs are at a range of ~€700-2000 kW⁻¹, AWE at ~€170–1000 kW⁻¹, while the cost of SOECs is around ~€3,000 kW⁻¹, even though SOECs only surpassed 1 MW of capacity installed in 2019. The minimum cost for alkaline electrolysers of \$300 kW⁻¹ is noteworthy, a value cited in several organizations relating to cost claims from recent Chinese manufacturing plants. However, it is essential to acknowledge that the costs of various electrolysers from different manufacturers are difficult to compare.

Costs differ substantially by technology due to design and materials requirements, as well as the maturity and scale of production. Prices vary strongly based on the country of manufacture, with a prominent disparity between China and the rest of the world. Prices are changing rapidly as manufacturers increase their scale of production.

A notable advantage in recent years is the significant and consistent reduction in the costs associated with electrolysers, spanning various technologies. Projections indicate that the CAPEX for large-scale electrolysers is set to decline by an impressive 40-50% within the next five years. To illustrate this progress, consider the remarkable cost reductions seen in two prominent electrolysis technologies: AWEs, which have plummeted from \$2000 to \$1200 kW⁻¹, and PEMWEs, which have similarly dropped from \$2800 to \$1400 kW⁻¹ over the same time frame.¹²

These cost declines can be attributed to several factors, primarily the maturation and expansion of the market, which has spurred advancements such as the scaling up of manufacturing, increasing plant sizes, enhancing design elements, and relocating production to more cost-efficient regions.



Figure 2-7 Historical and projected CAPEX costs for AWE, PEM, and SOEC technologies. Reproduced with permission from Reference.¹² Copyright The Royal Society of Chemistry 2022. Available under <u>Creative Commons Attribution 3.0 Unported Licence</u>.

2.2.4 Cost of water pre-treatment

Water impurities substantially impact the durability of electrolyser stacks, inflating the cost of hydrogen production. This longevity extension affects hydrogen pricing by contributing to the electrolyser's annuity. Impurities in water significantly influence the lifespan of all existing electrolyser technologies, a topic further elucidated in Section 4.1, **"Impact of Wastewater Impurities on Electrolysers"**. Aside from desalination expenses, any water treatment within the electrolyser stack incurs extra charges. These supplementary costs become particularly significant by escalating required water purity levels.

With the current electrolysis technology, water treatment is a necessary procedure before the electrolysis to produce hydrogen. The water treatment strategy depends on water sources, possibly from WWTPs, rainwater, seawater, cooling towers, surface water (rivers, streams, or lakes), and groundwater.³⁹ The dominant water treatment technology for hydrogen electrolysis is the reverse osmosis (RO) based process, which utilizes a semi-permeable membrane to eliminate ions, undesired molecules, and larger particles from water. It is important to note that advanced treatment methods, such as RO, tend to be more energy-intensive and can result in significant water loss, with the RO process alone leading to a loss of 20-30% of the input water.⁴⁰ A technical-economic analysis of the estimated cost of RO purification treatment before electrolyser input is shown in Appendix Table 2-4.³⁹ This analysis considers two distinct water sources: coastal areas and rural areas. The cost estimates encompass CAPEX and operations expenditures (OPEX) for pre-treatment of low-grade water for electrolysis across various potential water sources, including the coast area next to the urban area and the rural area situated 32 km from the coastline with minimal industrial facilities). CAPEX covers elements such as abstraction/collection, water transport, water pretreatment, storage, and water treatment waste disposal. Meanwhile, OPEX factors in waste disposal expenses, electricity costs for water retreatment operations and pumping during water transport, water charges, and labour costs. In addition, pre-treatment is mainly needed for RO technologies to minimise membrane fouling, which causes additional costs, particularly when using low-grade water as the feed. In conclusion, the analysis suggests that pre-treating surface water, encompassing creeks, streams, rivers, and lakes, is the most cost-effective approach for supplying water to electrolysers in coastal areas.

Note: The technical-economic analysis is based on a 700 m³/day of processed capacity with an energy need of 3-6 kWh/m³ for RO pre-treatment. The obtained water quality is deionised water with a conductivity of <5 μ S/cm.

Chapter 3. Status of Wastewater Treatment in Australia

3.1 Distribution patterns and associated contaminants in WWTPs

3.1.1 Distribution of WWTPs in Australia The presence of efficient sewage treatment facilities is crucial for a country as it not only safeguards public health by preventing the spread of waterborne diseases but also protects the environment by ensuring the responsible and sustainable disposal of wastewater. About 85% of the population in Australia has the opportunity to utilize over 700 community sewage treatment facilities, including nearly 350 biological filterbased plants, around 170 lagoon-based plants, and 45 primary treatment-based plants. The activated sludge process is stated as the method of choice for the majority of newly implemented plants.⁴¹ This comprehensive sewage treatment infrastructure underscores Australia's dedication to maintaining a clean and sustainable environment, fostering a high quality of life for its citizens while setting an example for responsible water resource management on a global scale. The strategic distribution of wastewater treatment plants across Australia ensures widespread coverage, effectively addressing the sanitation needs of diverse communities while promoting environmental stewardship and sustainable water management practices. The nationwide WWTP map, as depicted in Figure 3-1, provides a vivid illustration of their geographical distribution. The geographic distribution of WWTPs in Australia reflects the population distribution, environmental

considerations, and water resource management strategies unique to each region. Here's a general overview:

Urban Centres: Major cities such as Sydney, Melbourne, Brisbane, Perth, and Adelaide have large, advanced WWTPs designed to handle the significant volumes of wastewater produced by densely populated areas. These facilities often have sophisticated treatment technologies to meet strict environmental and water quality standards.

Coastal Areas: Along the Australian coast, where population density tends to be higher, there are numerous WWTPs to manage the wastewater while protecting the coastal and marine environments. These plants are crucial for preventing pollution of beaches and marine ecosystems, which are vital for tourism, recreation, and biodiversity.

Inland and Rural Areas: Inland towns and rural communities are served by smaller WWTPs or decentralized wastewater treatment systems. These facilities are designed to meet the needs of smaller populations and are often tailored to local environmental conditions and water availability. The distribution of WWTPs also varies by state and territory, with differences in the number, size, and technology of facilities reflecting regional water management policies, climate conditions, and specific environmental challenges. For example, areas with scarce water supplies may integrate water recycling and reuse practices more extensively.



Figure 3-1 National map of Australian wastewater treatment plants. Source: Commonwealth of Australia (Geoscience Australia) 2016.

3.1.2 Quality indicators of wastewater

The quality of influent wastewater to WWTPs depends on the type and concentration of contaminants. Temperature, colour, turbidity, and electrical conductivity are classified as water characteristics rather than contaminants. Wastewater quality indicators can be divided into Physical, Chemical, and Biological categories. A few examples for each category are listed and discussed below.

Physical: Total Solids (TS), Total Suspended Solids (TSS) and Total Dissolved Solids (TDS).

- Chemical: Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Total Nitrogen (TN), and Total Phosphorus (TP).
- 3. *Biological:* Total coliform, faecal coliform, and Escherichia coli (E. coli).

TS, TSS, and TDS: All these are crucial terms in wastewater treatment, each representing different forms of solids present in influent wastewater. TS encompass all particles, including algae, silt, clay, minerals, salts, and metals, whether dissolved, suspended, or settleable. Among these, TSS refer to particles large enough to be retained by a filter with pore sizes typically around 2 microns, while TDS are particles small enough to pass through

the filter. TSS is a critical parameter for assessing the quality of treated wastewater samples, offering insights into their overall condition post-treatment. TDS comprises a diverse range of inorganic and organic compounds dissolved in water, originating from various sources such as natural sources, industrial activities, agricultural runoff, and urban runoff. Examples of dissolved solids commonly found in TDS include minerals like calcium, magnesium, sodium, and potassium ions and bicarbonate, sulphate, chloride, nitrate, and phosphate ions. TDS measurements are closely related to conductivity, salinity, alkalinity, and hardness measures, making them essential for maintaining desired effluent qualities.

BOD: It is crucial for assessing water quality. It indicates how much oxygen microorganisms use to decompose organic substances in a sample. BOD is measured as the oxygen consumed per unit volume of the sample, usually at 20°C, over a set period, typically 5 days (known as BOD₅). This test reveals the activity of microorganisms breaking down organic compounds in the sample, expressed as mg of oxygen per litre.^{42, 43} BOD₅ is vital for ensuring wastewater discharge and treatment processes meet regulatory standards. It also helps determine the biodegradable portion of effluent in treatment plants. BOD₅ to COD (Chemical Oxygen Demand) provides insights into effluent biodegradability, while the COD/BOD₅ ratio helps size wastewater treatment plants effectively for specific locations.⁴²

COD: It is often preferred as an alternative to BOD in certain situations because it provides faster results. While BOD measures the amount of oxygen microorganisms consume during biochemical processes, COD measures the amount of oxygen needed for chemical oxidation. Standard methods for measuring COD in water use chemicals like toxic chromium (VI), mercury(II), and silver(I) to prevent common interference from chloride (the natural environmental processes don't oxidize chloride). Unfortunately, using these harmful chemicals in reagent formulations leads to environmental pollution, and such methods are not recommended in environmental studies. Fortunately, modern methods no longer rely on these substances and yield reliable results showing strong correlations compared to traditional standard methods.⁴⁴

TOC: The primary factor in determining the total amount of organic compounds in water is TOC. Carbon components typically originate from either natural organic matter or synthetic sources like materials and systems utilized for water purification. Also, this parameter is highly beneficial for detecting variations in the organic content during a treatment process.

TP: TP quantifies the total phosphorus content present in a sample, encompassing both dissolved and particulate forms. Excessive amounts of phosphorus lead to eutrophication in surface water bodies as phosphorus stimulates the growth of algae and aquatic plants. The increased biological activity due to phosphorus can lead to oxygen depletion in the water, causing negative impacts on aquatic ecosystems and human health. Therefore, it is essential to eliminate phosphate from wastewater before releasing it into the environment.

TN: TN represents the total quantity of nitrate (NO₃), nitrite (NO₂), ammonia (NH₃), and organic nitrogen, all expressed in terms of Nitrogen (N). However, TN is occasionally used as a regulated parameter for WWTPs, while more frequently, regulations specify limits for individual forms of nitrogen. Reducing the amount of TN in water has become a significant objective for both municipal and industrial wastewater treatment plants.⁴⁵

3.2 Wastewater treatment processes

Australia allocates approximately \$6 billion annually for water and wastewater treatment services. Within this budget, around 20% is dedicated to direct capital acquisitions and equipment maintenance.⁴¹ Wastewater is commonly categorized into four main types: (1) rainwater, which consists of runoff from impermeable surfaces, (2) municipal wastewater, (3) agricultural wastewater, and (4) industrial wastewater.^{46, 47} Rainwater availability fluctuates significantly, making it an unreliable source. The collection of agricultural wastewater presents substantial challenges due to its diffuse nature. Industrial wastewater exhibits considerable fluctuations in quality over time. Consequently, municipal wastewater emerges as the most viable option for hydrogen production, owing to its consistent availability and relatively uniform quality. Although 99.9% of municipal wastewater is water, hazardous contaminants must be removed before releasing them to the environment or other potential applications.

The municipal wastewater treatment process in WWTPs typically involves four consecutive stages, as outlined in Figure 3-2. Those stages, in order, are preliminary treatment, which employs physical and mechanical methods (e.g., screening and grit removal); primary treatment, involving physicochemical and chemical processes (e.g., clarification); secondary treatment, utilizing mainly biological but also physical and chemical means (e.g., aeration); and tertiary treatment, employing physical and chemical processes (e.g., advanced oxidation, membrane filtration). Tertiary treatment is considered an optional stage in the wastewater treatment process, implemented specifically to achieve higher levels of contaminant removal for producing water of elevated quality. This advanced treatment step is employed when the desired water quality standards necessitate removal efficiencies beyond what primary and secondary treatments can achieve. Simultaneously, handling sludge gathered in the sedimentation tanks during the primary and secondary processes relies on anaerobic digestion.



Figure 3-2 General overview of the water treatment processes in WWTPs in Australia. (Source: Water Corporation Australia)⁴⁸

2.2.1 Preliminary treatment

Preliminary wastewater treatment aims to remove coarse solids and other large materials commonly present in untreated sewage. This process focuses on eliminating or reducing the size of sizable, suspended, entrained, or floating solids, including wood, cloth, paper, plastics, and debris. Inorganic solids like sand and gravel, along with metallic or glass materials, are also removed while fulfilling the requirement of eliminating grit and excessive quantities of oils and greases.⁴⁹

At a WWTP, specialized bar screens are used to capture and remove large objects from the incoming wastewater, serving as a standard pretreatment method to promote uniformity in wastewater composition and prevent damage to equipment. After bar screening, the wastewater passes through a grit chamber to eliminate heavy solids like sand and gravel further, which can also cause machinery damage. The reduced flow velocity in the grit chamber aids in separating grit material, consisting of non-decomposing solid substances with a higher density than organic solids, typically characterized by a density ratio ranging from 2.4 to 3.0. ⁵⁰ Considering that only large suspended particles are removed, the water quality after the preliminary treatment step is still quite low.

2.2.2 Primary treatment

The primary treatment uses physical methods like sedimentation and flotation to remove organic and inorganic solids. This process successfully eliminates about 25-50% of the initial BOD₅, 50-70% of the TSS, and 65% of the oil and grease. It also removes certain organic nitrogen, phosphorus, and heavy metals linked to solids during the primary sedimentation phase. However, colloidal and dissolved components remain unaffected at this stage.⁴⁹ After settling in the primary treatment, the clarified water undergoes further treatment processes. Following this phase, the wastewater will be devoid of particles exceeding 10 μ m in size and should primarily consist of organic substances. The primary effluent could be suitable for irrigation but not for human consumption.

3.2.3 Secondary treatment

Secondary treatment in WWTPs plays a pivotal role in the removal of biodegradable organics, primarily assessed through the reduction of BOD and COD. This stage employs biological processes that utilize microorganisms to degrade organic pollutants dissolved or suspended in wastewater. By converting organic matter into biomass and gases, secondary treatment significantly lowers the levels of BOD and COD, indicators of the organic pollutant load in the water. The wastewater effluent is initially directed into a stirred and aerated basin for secondary treatment, as depicted in **Figure 3-3**. Air is introduced into the basin as bubbles emanating from the bottom to supply oxygen to microorganisms.

Effective secondary treatment processes can achieve high removal efficiencies for both BOD and COD, typically ranging from 85% to 95% for BOD and similarly high rates for COD, depending on the specific technologies and operational conditions employed.⁴⁹



Figure 3-3 Illustration of a secondary wastewater treatment system.

3.2.4 Tertiary treatment

Tertiary treatment, which comes after the standard secondary treatment in the wastewater treatment process, incorporates advanced treatment techniques to improve treated water quality further by removing specific contaminants. Commonly used technologies for tertiary treatment include filtration, to remove particles physically; membrane processes, such as RO, which can remove dissolved salts and microscopic pollutants; advanced oxidation technologies (AOTs), for breaking down complex chemicals into simpler, less harmful compounds; and disinfection methods, like chlorination or ultraviolet (UV) light exposure, to eliminate pathogenic microorganisms. These technologies are selected based on the specific treatment goals, the nature of the effluent, regulatory requirements, and economic considerations. However, their widespread adoption is hindered by the high costs associated with the treatment.49

AOTs effectively remove persistent and hard-todegrade organic pollutants, which can't be removed in the secondary treatment stage.⁵¹ The most commonly used AOTs include *a*) *Ozonation*, which uses ozone as a strong oxidizing agent to break down pollutants. It's effective against a wide range of contaminants, including bacteria and viruses, and can also help in colour and odour removal; b) UV Radiation: UV light, especially when combined with hydrogen peroxide (H_2O_2) , can produce hydroxyl radicals (•OH) capable of degrading organic compounds;⁵² c) Fenton's **Process:** Involves the reaction of hydrogen peroxide with iron salts (Fenton's reagent) to generate hydroxyl radicals. *d) Electrochemical* **Oxidation:** This involves using an electric current to generate reactive species directly on the electrode surface or through the electrolysis of water. This method is suitable for the mineralization of organic pollutants. Each method has its advantages and limitations, including efficiency in pollutant removal, operational costs, and potential generation of secondary pollutants. Together, AOTs offer a versatile and effective toolkit for enhancing water quality through the tertiary treatment of wastewater.

Membrane technologies, particularly RO, have emerged as pivotal in the tertiary treatment of municipal wastewater, showcasing unparalleled proficiency in purging a comprehensive spectrum of contaminants. At the core of RO technology is utilising a semipermeable membrane engineered to allow the passage of water molecules while obstructing unwanted substances. As illustrated in **Figure 3-4**, this filtration mechanism is driven by applying pressure that surpasses the osmotic pressure, compelling water molecules through the membrane and leaving behind a wide array of impurities, including salts, microorganisms, organic compounds, and trace pharmaceuticals.

The resulting water from the RO process is of exceptionally high quality, making it suitable for a myriad of applications ranging from industrial and agricultural use to replenishment of potable water supplies. This adaptability underscores RO's significance in addressing critical water quality and scarcity challenges, bolstering water security and sustainability efforts. Furthermore, advancements in RO technology have led to more energy-efficient systems and reduced operational costs, enhancing its feasibility for widespread use. Membrane fouling, a common challenge associated with RO systems, is being addressed through innovative pre-treatment processes and the development of more resistant membrane materials, extending the lifespan of the system and maintaining its efficiency. The integration of RO in tertiary treatment is a testament to the ongoing efforts in water treatment technology to achieve sustainability, resource recovery, and environmental protection, making it a critical component of modern water management strategies.



Figure 3-4 Mechanism of RO separation technique

3.3 The quality of treated wastewater from Australian WWTPs

Understanding how successive treatments affect the water quality is significant for effectively managing the quality before introducing that to electrolysis. As elaborated in the previous section, the four stages of wastewater treatment contribute to a continuous improvement in water quality. **Appendix Table 3-1**⁵³ summarizes the effectiveness of each treatment process in reducing specific contaminants.

Aiming to evaluate the ability of green hydrogen production and provide a reference for further upgrades of the WWTP facilities, we collected data on historical water quality over the last three years provided by four typical WWTPs through WaterRA (Appendix Table 3-2). Analysis of the impurity concentrations from the tertiary effluent depicts that tertiary effluent aligns more closely with the required water quality for electrolysis (further detailed in Chapter 4). A notable observation is that Class A and secondary effluents exhibit markedly higher concentrations of common metal cations and chlorine anions than tertiary effluent. This disparity is also reflected in the elevated electrical conductivity. Of significance, the substantial presence of metal cations could potentially contribute to cathode degradation,

whereas the anions pose a notable risk of anode poisoning.

In light of effluent water quality monitoring from the WWTPs, it's evident that supplementary purification or advanced wastewater treatment remains imperative to uphold the required element levels within specified parameters. Further recommendations for additional purification measures will be elaborated upon in **Chapter 6**, offering a comprehensive perspective on potential solutions to ensure the feasibility of sustained hydrogen production.

The evidence indicates that tertiary-treated effluent, such as that from the Beenyup Advanced Water Recycling Plant (Figure 3-5), holds promise as a potential feedstock for electrolysis, with experimental use yielding encouraging results. Notably, hydrogen production from these treated wastewater samples has, in several instances, exceeded that of distilled water (Figure **3-6**). Despite these positive outcomes, it is essential to conduct long-term studies to thoroughly understand the potential impacts of residual impurities present in treated wastewater on the efficiency and longevity of water electrolysis systems. It is this understanding that will be critical in assessing the viability of utilizing treated wastewater for sustainable hydrogen production at a larger scale.



Figure 3-5 Overview of the tertiary wastewater treatment at Beenyup WWTP. (Source: Water Corporation Australia)⁴⁸



Figure 3-6 Hydrogen production test on electrolysis of tertiary water samples from Beenyup Advanced Water Recycling Plant (AWRP): (a) current from a PEMWE electrolyser charged by -2 V. Hydrogen flowrate and corresponding (b) hydrogen flow rate.

Furthermore, untapped tertiary water effluents harbour a substantial potential for scaling up green hydrogen production. Analysis of Sydney Water's wastewater treatment plants by Aguey-Zinsou et al.⁵⁴ shows that plants have 37.6 ML/day of unused tertiary effluents (see **Appendix Table 3-**

 $\mathbf{3}^{54}$), which, if electrolysed, would generate 420,000 t H₂/day or 0.88 Mt H₂/year and cover ~100% of Australia's estimated production by

2030. Sourcing hydrogen from recycled effluents would support a circular economy approach by keeping resources in use and avoiding waste.

Chapter 4. Water quality gaps

4.1 Impact of water impurities on electrolysers

Impurities in the water used for electrolysis can significantly affect electrolysers' performance, efficiency, and longevity. These impurities, as categorised above, can affect the different electrolyser parts as follows;

- Cations such as Na⁺, Ca²⁺, and Mg²⁺ can replace protons in the membrane of a PEMWE, leading to reduced conductivity and efficiency.
- Anions like Cl⁻, Br⁻, and SO₄²⁻ can cause corrosion of the electrolyser components, particularly under high-potential conditions at the anode.
- Organic Molecules can form films on the catalyst surface, blocking active sites and reducing the reaction rate.

The presence of impurities in water used for hydrogen electrolysis can significantly impact the efficiency and longevity of the electrolysis system. Hydrogen electrolysis involves splitting water into hydrogen and oxygen gases by passing an electric current through it, typically using a catalyst-coated electrode. The impact of impurities on this process can be multifaceted:

- *Catalyst Poisoning*: Impurities can adsorb onto the surface of the catalysts (e.g., platinum, iridium) used in the electrolyser, hindering the access of water molecules to the active sites. This phenomenon, known as catalyst poisoning, reduces the efficiency of the electrolysis reaction and decreases the hydrogen production rate.
- *Increased Corrosion*: Impurities may contribute to the corrosion of the electrolyser components, especially the electrodes and the membrane. Corrosion can lead to the deterioration of these

components, reducing the system's overall efficiency and lifespan.

- Membrane Fouling: In PEM electrolysers, impurities can lead to membrane fouling. This fouling can decrease the membrane's ionic conductivity and increase the cell's electrical resistance, leading to a drop in efficiency and an increase in energy consumption for the same hydrogen output.
- Operational Instability: Accumulation of impurities can cause fluctuations in the electrolysis process, leading to operational instability. This can manifest as variations in the current density and electrolyte conductivity, which can further impact the efficiency and stability of hydrogen production.
- Maintenance and Operational Costs: The presence of impurities necessitates more frequent maintenance and replacement of parts, leading to higher operational costs. It may also require the installation of additional treatment processes to purify the water before electrolysis, further increasing the costs.

PEMWEs, AWEs, and AEMWE water electrolysers are sensitive to water quality, with a range of common impurities impacting performance, hydrogen quality, and device lifetime. Understanding the impact of water impurities on the performance and durability of electrolysers is necessary to electrolyse wastewater to produce low-cost hydrogen to meet the market demand. **The electrolyser manufacturers typically specify a minimum required water supply quality in terms of conductivity, typically <1** μ S cm⁻¹ (>1 M Ω cm). In Australia, there is no searchable protocol for water quality for testing water electrolysis. The EU water electrolyser testing guidelines from the Joint Research Centre call for ISO 3696 Grade 2 water, which has a conductivity of <1.0 $\mu S~cm^{-1}$ at the inlet and for PEM electrolysis. $^{13,~55}$

To understand and mitigate the effects of impurities, various analytical techniques can be utilised as follows: For postmortem analysis, SEM/EDX (Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy) can be used to map the distribution of impurities within the cell after disassembly. If used, XPS (X-ray Photoelectron Spectroscopy) and EPMA (Electron Probe Microanalysis) offer surface-sensitive analysis and can detect impurities down to ppm levels. ATR-FTIR (Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy) can investigate changes in functional groups within the membrane and the impact of contaminants. Additionally, In Situ and Operando Techniques are vital in pinpointing the real-time effect of these impurities on hydrogen production in the electrolysers. For example, neutron imaging can show the distribution and behaviour of impurities within the cell during operation. Although it is limited to ions with a sufficient neutron scattering cross-section, ICP-MS (Inductively Coupled Plasma Mass Spectrometry) allows for trace element analysis of liquid solutions, which is crucial for detecting and quantifying impurities in the electrolyte, SFC ICP-MS (Scanning Flow Cell Inductively Coupled Mass Spectrometry) couples electrochemical flow cell and ICP-MS to determine the composition of the electrolyte as a function of electrochemical properties.

4.1.1 Impact of impurities on AWEs and AEMWEs

The impact of impurities AWEs and AEMWEs is a critical area of study, as these impurities can significantly influence the performance and longevity of these devices. The effect of the different types of impurities on AWEs and AEMWEs is summarized in **Appendix Table 4-1 and Figure 4-1** and detailed in various subcategories as follows.

Cationic Impurities. In AWEs and AEMWEs, cations do not directly threaten the membrane or ionomer as they do in PEMWEs, as the leading charge carriers are anions, particularly hydroxide ions (OH⁻). However, certain cationic impurities found in water and potassium hydroxide electrolytes can either enhance or diminish the performance of OER catalysts, depending on their nature. For instance, Ni²⁺ and Fe²⁺ can enhance OER catalyst performance,⁵⁶ while Zn²⁺, Cd²⁺, and Pb²⁺ can decrease performance upon adsorption.⁵⁷⁻ ⁶¹ Additionally, Ca²⁺ and Mg²⁺ cations may deposit at high pH, potentially blocking reactant access to catalyst sites.

Anionic Impurities: Anionic impurities pose a significant threat in both AWEs and AEMWEs due to the reliance on anions as charge carriers. For example, carbon dioxide (CO₂) from ambient air can react with potassium hydroxide to form bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) anions, leading to decreased ionic conductivity and performance. If introduced from impure feed water, halogen ions, particularly chloride (Cl⁻), can cause unwanted side reactions and potential electrode corrosion.



Figure 4-1 Summary of the impact of impurities on AEMWEs (top) and AWEs (bottom). Reproduced with permission from Reference.¹³ Copyright The Royal Society of Chemistry 2022. Available under <u>Creative Commons Attribution 3.0 Unported Licence</u>.

Organic Impurities. The impact of organic impurities on AWEs and AEMWEs remains less understood, with questions remaining about their effect on performance and catalyst durability. Organic impurities introduced from lower-quality water are expected to be oxidized at the anode into various products depending on the applied potential, potentially contaminating the hydrogen product and necessitating additional purification processes.

Inert Impurities. The highly alkaline environment of AWEs and AEMWEs can cause precipitation of metallic ions due to the low solubility of their oxides and carbonates, potentially causing clogging and mass transport issues.

Despite the advances in understanding the effects of various impurities on AWEs and AEMWEs, there remains a significant knowledge gap regarding the specific impacts of impurities at the single-cell or stack level of these systems. Furthermore, the interaction of organic impurities and the challenge of optimizing electrodes for OER selectivity in environments containing chloride anions—critical for the development of direct seawater electrolysis and the use of lower-quality water to reduce purification costs—are areas that are not fully understood. While AWEs have demonstrated resilience against trace impurities, the detailed effects on the performance and longevity of modern, high-performing devices are still being explored. Thus, a deeper comprehension and mitigation of impurity impacts are essential to enhance the efficiency, performance, and durability of both AWEs and AEMWEs, paving the way for more sustainable and cost-effective electrolysis solutions.4.1.2 Impact of impurities on PEMWEs

Poor water quality is one of the main reasons for stack failure for PEMWEs, although with these electrolysers, reported lifetimes go over 50,000 hours.¹³ The factors affecting their lifetime are not limited to poor water quality alone but also their operating conditions, voltage fluctuation, gas leaking, and anode dissolution. Nevertheless, many electrolyser components are quickly affected due to impurities such as membranes, ionomers in the catalyst layer, catalysts, and porous transport

layers. The type of impurity, possible route of entry, and impact on PEMWE components are summarised in **Appendix Table 4-2**.

Cationic Impurities. Cationic impurities, primarily originating from the feed water, are particularly problematic for PEMWEs. They can substitute protons within the membrane and ionomer, decreasing proton pathways and reducing electrochemical reaction rates. In the membrane, these cations replace charge carriers with less mobile ions, thus lowering the ionic conductivity. Iron cations can also initiate the Fenton reaction, causing membrane degradation. Cations can act as poisons at the catalyst layer, reducing activity and enhancing dissolution.

Anionic Impurities. These are mainly sourced exogenously except for F^- and SO_4^{2-} , which are membrane degradation products. Anions are less damaging than cations as they cannot substitute protons. However, they can still adsorb on the catalyst surface, reducing activity.⁶² Chlorides are the most widely studied anions due to their presence in seawater and tap water. They can be oxidized into chlorine at the PEMWE anode, leading to secondary damage to tubing and ancillary equipment and contamination of product gases. Hence, halide ions pose a risk by adsorbing on the catalyst surface and in the case of I⁻ and Br⁻, this may be irreversible at sufficiently high concentrations. The strength of halide ion adsorption follows the order $I^- > Br^- > Cl^-$.Other anions can also be adsorbed on the catalyst, but the low potential at the cathode and high potential at the anode usually prevent significant issues. Sulphate (SO₄²⁻) and bisulphate (HSO₄⁻) anions are other by-products of membrane degradation. SO₄²⁻ adsorption is a function of potential. At the anode, SO_4^{2-} at a high 0.05 M has been shown to adsorb on Ir and shift the onset of the OER to higher potentials.⁶²

Organic impurities. While less studied, they can adsorb on the catalyst surface, blocking active

sites and enhancing catalyst dissolution. The oxidation of organic molecules at the anode can produce carbon monoxide and carbon dioxide, which can cross over to the cathode, lowering hydrogen quality and poisoning the cathode catalyst. The impact of organic impurities on the performance and stability of the catalyst layer is a concern, particularly as using lower-quality water could simplify water purification processes or reduce the energy required for hydrogen production.

Inert impurities. These are solid inert particles that could potentially lead to mass transport issues. They may be introduced into the water from external sources and/or failure of the water purification system. These particles can accumulate and block the membrane pores, leading to mass transport problems. For instance, the circulated water running in a PEMWE showed a pronounced increase of silicon after a hundred hours of operation, likely originating from the nano-silica-filled polypropylene tank.^{13, 63}

In summary, a couple of overarching challenges emerge in this regard. The ongoing development of AEMWE systems complicates studies, leading to a lack of consensus on materials, designs, and operations. One primary challenge is evaluating how low concentrations of impurities affect the lifespan of electrolysers used in practical settings. While many studies focus on high-concentration impurities for quicker observations, real-world systems endure extended periods (likely 10,000 hours) with lower impurity levels. Without longterm data on these lower concentrations, understanding the actual effects of impurities and their degradation mechanisms is difficult. Another challenge involves improving the precision and frequency of measurement techniques to explore degradation mechanisms. It's crucial to capture transient operations, which often cause the most notable cell degradation. Traditional methods like standard ICP-MS suffer from low time resolution due to manual sampling. In contrast, techniques

like SFC ICP-MS offer higher temporal resolution, enabling better identification of potential transients.^{13, 64}

4.2 Impact of impurities on the cooling system

The impact of impurities on the cooling system within green hydrogen facilities is critical as well due to its fundamental role in maintaining optimal operating conditions and overall efficiency. While ultrapure water remains essential as a feedstock, determining the appropriate amount of cooling water poses challenges, especially as various projects employ different cooling methods. For instance, smaller initiatives often utilize dry cooling techniques, while larger-scale electrolysis systems may integrate surplus heat into existing waterbased infrastructure or rely on seawater for cooling.⁶⁵ However, regardless of the cooling method employed, impurities present in the water can lead to various detrimental effects on the system's performance.

Impurities such as calcium, magnesium, and chlorides can cause significant issues within the cooling system. Calcium and magnesium can precipitate and form scale on heat exchanger surfaces, hindering heat transfer and potentially causing overheating. Conversely, chlorides can corrode metals used in cooling systems, leading to component degradation and failures. Additionally, organic impurities and biological components can foster the growth of microorganisms, resulting in biofouling, which can clog cooling channels and further reduce heat transfer efficiency. Moreover, particulate matter and other solid impurities may accumulate, obstructing pipes and channels and diminishing cooling capacity.

The specific design of the cooling system plays a crucial role in determining water usage and addressing impurity-related challenges. Key considerations include initial water quality, the balance between conductive and evaporative

cooling, drift ratio, and concentration factor. While obtaining precise figures can be complex due to these variables, a rough estimate suggests approximately 400 litres per hour of cooling water per megawatt electrolysis capacity, roughly double the amount required for electrolysis.⁶⁵ Recognizing the distinct quality requirements for cooling water compared to electrolysis water ensures optimal system performance and longevity.

Effectively managing impurities within the cooling system is imperative for sustained operational integrity and environmental responsibility. Strategies to address impurity-related challenges include employing chemical, physical, and biological treatment processes to maintain water quality. Additionally, managing the cycle of concentration within the cooling water loop can help mitigate issues such as scale formation, corrosion, and biological growth, thus contributing to the overall efficiency and sustainability of the cooling infrastructure.⁶⁶ Moreover, the auxiliary circulation water loop plays a crucial role in enhancing thermal control and mitigating temperature fluctuations, thereby safeguarding the system's longevity and performance, especially in the context of increasing current densities in electrolysis systems.67,68

4.3 Economic viability of WWTPs-based hydrogen economy

Creating cost-effective green hydrogen remains a challenge today, with the Australian Government directing funding towards the cost reduction and stimulating its adoption. Based on the Australian Renewable Energy Agency analysis, Australia has identified that hydrogen must be priced below AU\$ 2 kg⁻¹ to compete with alternative energy sources. However, the present capital cost of green hydrogen sits at AU\$ 4-6/kg (US\$2.76-4.14/kg), depending on which renewable energy and electrolyser are used for electrolysis.⁶⁹
4.3.1 High cost of hydrogen

Reducing the cost of hydrogen to reach the AU\$ 4-6/kg price range remains a major barrier to widespread adoption. The two most important hydrogen cost drivers are the electrolyser manufacturer's CAPEX and the electrolysis system's OPEX for electricity. As with many areas in the energy sector, CAPEX plays a defining role in the overall economic viability of hydrogen electrolysis. As stated in Chapter 2, The cost contribution of various elements in water electrolysis systems varies widely across the literature. For example, IRENA calculates that the stack contributes to 45% of the total system cost.⁹ The remainder comes from the balance-ofplant components: electricity supply (28%), water circulation (12%), hydrogen processing (11%) and cooling (4%).⁹ Mayyas and Mann similarly model the stack as contributing 40% of the total system cost, with the BOP share mostly coming from the power supply. All in all, the CAPEX of electrolyser stacks is prominent in the cost distribution.⁷⁰

Currently, hydrogen production via water electrolysis is more expensive than with other methods due to the capital costs and dependence on electricity costs. Although the CAPEX and OPEX of electrolysers have been reduced noticeably since 2012, further improvements are required, primarily when operated solely on renewable energy sources. It is worth noting that new hydrogen production technologies are being developed, and established technologies are undergoing continual refinement. Combined with the rapid scale-up of manufacturing, there is widespread expectation that current prices will continue to fall.

Utilizing wastewater in processes offers a costeffective reduction in water usage, yet it may introduce additional CAPEX and OPEX. This dualedged effect arises because, on one hand, recycling wastewater can significantly lower the costs associated with freshwater acquisition, contributing to sustainable resource use and potentially offering economic advantages in the long term. On the other hand, the initial investment in technology and infrastructure required to treat and recycle wastewater effectively can be substantial. This includes costs related to installing advanced treatment systems, which are necessary to ensure the wastewater meets the required quality standards for reuse.

Moreover, operational costs may increase due to the need for ongoing maintenance, energy consumption, and management of these advanced systems. The complexity of treating various contaminants present in wastewater, such as organic materials, heavy metals, and emerging pollutants, further complicates the process, potentially requiring a multi-stage treatment approach and, consequently, higher operational costs.

Despite these financial considerations, the longterm benefits of wastewater reuse, including reduced demand for freshwater resources, the potential for cost savings in water-intensive industries, and contribution to environmental sustainability, often justify the initial investment. It becomes crucial for organizations to conduct thorough cost-benefit analyses, considering both the immediate financial outlays and the long-term economic and environmental returns, to make informed decisions regarding the integration of wastewater reuse into their operations.

4.3.2 Expenses of upgrading WWTP infrastructure

In the Australian context, where water scarcity is a pressing issue in many regions, the expense of upgrading wastewater treatment plant infrastructure for green hydrogen production must also consider the water footprint of electrolysis processes. Utilizing wastewater as a feedstock for green hydrogen production can mitigate some of these concerns by repurposing treated wastewater that would otherwise be discharged into the environment. However, ensuring the quality of water used in electrolysis processes may require additional treatment steps, increasing both capital and operational costs. Balancing the water requirements of green hydrogen production with existing demands for agriculture, industry, and urban consumption will be essential in managing costs and ensuring sustainable water management practices.

Upgrading wastewater treatment plant infrastructure for green hydrogen production poses both potential expenses and significant benefits.⁷¹ The initial capital investment required for retrofitting existing wastewater treatment facilities to accommodate green hydrogen production processes can be substantial. Different WWTPs will face different conditions and potential cost savings. It is imperative to delve into two pivotal inquiries: firstly, the determination of whether a WWTP necessitates an upgrade, and secondly, the assessment of its access to cost-effective renewable energy sources.⁷² The WWTP infrastructure replacement or upgrade is necessary for aimed cost reduction. If the capital cost savings are insufficient to support the infrastructure upgrade, the economic viability of the WWTP-based hydrogen economy appears to have a limited probability of being substantiated. Standard upgrades include equipment, implementing new technologies for electrolysis, and enhancing water purification systems to ensure the production of ultrapure water, a critical component in electrolysis.

Additionally, operational expenses such as energy consumption for electrolysis and ongoing maintenance costs must be considered, potentially adding to the financial burden of these upgrades. However, these expenses should be weighed against the long-term economic and environmental benefits of green hydrogen production, including reduced greenhouse gas emissions, enhanced energy security, and the potential for economic growth by developing a sustainable hydrogen industry in Australia.

More importantly, navigating regulatory frameworks and obtaining necessary permits for upgrading wastewater treatment plant infrastructure can add complexity and potential expenses. Compliance with environmental regulations, water quality standards, and safety protocols may require additional investments in monitoring equipment, staff training, and regulatory compliance measures. However, proactive engagement with government agencies, industry stakeholders, and local communities can help streamline the permitting process and mitigate potential delays and expenses associated with regulatory compliance. Overall, while upgrading wastewater treatment plant infrastructure for green hydrogen production in Australia may entail significant expenses, the longterm economic, environmental, and social benefits can outweigh these costs, positioning Australia as a leader in the transition to a sustainable hydrogen economy. And without a national water strategy, there is no national hydrogen strategy.⁷¹

Chapter 5. Utilisation of electrolysis co-product in WWTPs

Oxygen is commonly produced as a by-product in water electrolysis for hydrogen production. However, this process can be tailored to produce other valuable oxidants, such as ozone and H₂O₂, instead of, or in addition to, oxygen. This modification can be achieved through specific catalysts or by further processing the oxygen output. Oxygen, ozone, and H₂O₂ are all valuable and have significant potential applications in wastewater treatment processes.

Ozone is known for its strong oxidative capabilities, making it effective in breaking down complex organic pollutants, disinfecting water, and removing odours and colours. Similarly, hydrogen peroxide is used for its oxidizing properties, offering benefits in pollutant degradation and disinfection without leaving harmful residues. Integrating such oxidants into wastewater treatment can enhance contaminant removal efficiency, contribute to the reuse of treated water, and improve overall environmental sustainability.

By optimizing the electrolysis process to coproduce these oxidants, there is an opportunity to generate hydrogen as a clean energy source and leverage the by-products for environmental management and water treatment applications. This dual-purpose approach can maximize the utility and value of the electrolysis process, presenting a compelling case for further research and development in this area.

5.1 Using pure oxygen in wastewater treatment

Replacing air (having approximately 21% oxygen content) in the aeration process of wastewater treatment with the by-product oxygen (high purity - more than 99% of oxygen)⁷³ from hydrogen generation is presently under extensive discussion.

Efficient use of high-purity oxygen in WWTPs can aid in offsetting other energy consumptions. However, only a few studies have focused on integrating the two industries and using highpurity oxygen to assess the feasibility through pilot or full-scale applications, all with mixed outcomes (positive and negative conclusions).⁷⁴

The aerobic treatment process involves exposing wastewater to oxygen, promoting the growth of microorganisms that consume organic pollutants; within this category, the activated sludge process specifically utilizes a suspended culture of microorganisms in aeration tanks, enhancing the breakdown of organic matter and significantly contributing to wastewater treatment. Aerobic treatment in the wastewater treatment process plays a crucial role in breaking down organic contaminants, promoting efficient nutrient removal (e.g. nitrification), and ensuring the overall effectiveness of the treatment process, ultimately contributing to the production of environmentally safer effluent. Aeration has the highest energy consumption in wastewater treatment, responsible for 50%-60% of the total cost of plant energy usage.⁷⁵ As aeration is the constraining element in the wastewater treatment process, introducing oxygen can increase the entire system's capacity while enhancing its potential to reach new demands. ⁷⁶ It is significant to identify the utilization possibilities of high-purity oxygen as a by-product from hydrogen generation in aeration to optimize the wastewater treatment processes, enhance microbial activity, and improve the efficiency of organic matter decomposition.

High-purity oxygen can result in a tenfold rise in the quantity of dissolved oxygen within the digesters.⁷⁷ It has been identified that it is possible to apply by-product oxygen by compressing and storing it as an "oxygen battery" while replacing the traditional aeration having high energy consuming air blowers by the highly efficient, high-purity oxygen utilization methods in the activated sludge process (e.g. using a Speece cone). This innovative energy-shifting process demonstrates the capability of storing oxygen during periods of peak electricity availability and using it when the oxygen demand of the wastewater treatment plant surpasses the supply capacity from electrolysis.⁷⁴ It was determined that a 20% increase in the oxygen mass transfer coefficient and up to 30% energy return could be achieved by replacing air with by-product oxygen, focusing on oxygen mass transfer for a single bubble rising in stagnant water. Further, transferring from air to pure oxygen provides an elevated oxygen transfer rate with a higher driving force, which could be further be enhanced by facilitating small bubbles with the potential for shrinkage rather than expansion.⁷⁸ Having concentrated oxygen as a backup or a temporary supply to deal with unforeseen/high-demanding circumstances (such as weather events or societal events) is another intriguing utilization possibility of the by-product oxygen, enabling the plant to effectively elevate its capacity during such an emergency.76

In summary, we can draw the following essential observations comparing the utilization of air and Pressurized Oxygen (PO) in the activated sludge processes, primarily focusing on some crucial treatment parameters,^{79, 80} which can further assist in the decision-making process regarding the utilization of the by-product oxygen in the wastewater treatment.

 Oxygen concentration - A higher quantity of oxygen can be added to the process per time unit when using PO while reducing the risks (e.g. increase in the growth of filamentous bacteria, risk of foam formation, and increase in the sludge formation) due to having lower dissolved oxygen levels than expected (a minimum oxygen concentration of $1.1 \text{ mg O}_2/\text{L}$ is needed for the aeration).

- Oxygen transfer rate When using air, this is limited and directly related to the oxygen concentration in the air supply. Using PO can ensure elevated oxygen transfer rates with its high-purity oxygen content at low flow rates.
- Kinetics for microorganisms Increased kinetics can be observed when using PO, where a higher load of organics can be treated at a maintained sludge age.
- Mixed Liquor Suspended Solids (MLSS) – Higher MLSS concentrations can be accommodated using PO other than air.
- Removal Efficiency A larger amount of organic pollutants (with a higher variety) can be oxidized with elevated dissolved oxygen levels at low flow rates when using PO.
- Degradation of phenols and micropollutants – PO allows an increased ability for degradation compared to air.
- pH PO utilized activated sludge systems are sensitive to pH, especially the nitrification process and the inability to remove generated CO₂ from the system will decrease the pH level, which can affect the nitrification process.

It can be concluded that, provided optimal circumstances are met, and when contrasted with air delivery through blower systems, pure oxygen offers significant promise for enhancing aerobic water treatment processes. However, the fact that the MLSS content shouldn't be too low and that the sludge age must be maintained are limitations associated with the direct oxygen supply to the activated sludge process. Moreover, nitrification with oxygen at low temperatures may help overcome challenges in nitrifying wastewater.⁷⁹

Further, utilising by-product oxygen is beneficial in reducing high electricity consumption in the generation of oxygen through air-separation technologies like pressure swing absorption (PSA) and cryogenic air separation.⁸¹ Substituting air with the by-product oxygen can enhance a wastewater treatment plant's Net Present Value (NPV), which can be further increased by incorporating a photovoltaic (PV) system alongside grid electricity. Under the same analysis, in terms of the Levelized Cost of Hydrogen (LCOH), the additional use of the by-product oxygen indicated a reduction compared to having traditional airbased aeration, and it also emphasised that using the oxygen becomes more economically advantageous as the cost of electricity for operating water electrolysis increases. 73

The use of pure oxygen, with a pressure exceeding 500 kPa, compared to air (with 80 kPa pressure), may incur additional costs for retrofitting the air blowers.⁵ Further, it has been identified that replacing traditional aeration (having a lower oxygen transfer efficiency) with high-purity oxygen application can reduce the equipment sizes, including renewable electricity generation and electrolyser, for a given WWTP size four times less.⁷⁴ While upgrading the plant's capacity, this strategy can potentially exchange the upfront cost of concrete construction for the cost associated with introducing concentrated oxygen.

Because the clean hydrogen production cost using sustainable methods and renewable energy sources is well above the industrial hydrogen price, it is expected to make significant developments in clean hydrogen production technologies in the future with the aid of R&D works. Further, the direct utilization of oxygen in the aerobic stage needs to be studied more for its applicability, especially using pilot studies with major improvements in oxygen-feeding systems. The infrastructure capacity reduction possibilities associated with introducing high-purity oxygen to the aerobic systems need to be considered in future designs while finding the applicability of oxygen to the existing plants- an opportunity for capacity enhancement with the existing structures alone.

5.2 Ozone in wastewater treatment

Ozone exhibits robust oxidizing properties, which enable it to eliminate or neutralize pollutants and contaminants. The main objectives of using ozone in wastewater treatment include disinfection and removing dissolved organic matter. According to previous studies,⁸² ozone is a costly oxidant, and treating wastewater requires larger doses than natural water, which raises operating expenses. But ozone's capacity to mineralize organic matter—either by itself or in combination with other oxidants like hydrogen peroxide—makes it particularly appealing for novel developments, especially those whose goal is wastewater reuse.

Pure oxygen, the beneficial by-product of hydrogen generation, can be transformed into ozone, which can be utilised primarily in the wastewater treatment's disinfection stage.⁵ In line with contemporary methods, Corona Discharge or UV Light methods are used in producing ozone, and it has been highlighted that utilizing pure oxygen as the feedstock typically provides 2-3 times the output of dry air and 4-6 times the output of ambient air.⁵² The electrochemical production of ozone is also under consideration. However, as it is still in the early phases of development, more work needs to be done before reaching high technological readiness levels.83 Considering oxygen as the feedstock, it has been mentioned that the ozone can be produced from either liquid oxygen (LOX) or fed with oxygen gas (PSA system).⁷⁹ Concentrated oxygen (with a minimum of 90% oxygen and moisture removed) produced from an oxygen concentrator or delivered from an oxygen cylinder provides numerous benefits compared to the use of

ambient or dry air for ozone generation, including elimination of corona cell maintenance and higher concentration facilitating elevated solubility of ozone in water.⁵² Consequently, it is certain that the by-product oxygen from hydrogen generation which has more than 99% oxygen⁷³ has the ability to maximize the aforementioned advantages while eliminating/minimizing the disadvantages associated with using concentrated oxygen produced from air flow such as high-cost inquired due to the more equipment usage like oxygen concentrators and use of high complex systems for ozone generation.⁵²

Facilitating a proper gas/liquid contact mechanism to ensure efficient ozone transfer is significant for adequate ozonation. Ozone transfer using bubble diffusion and ozone injection via venturi injectors are popular mechanisms to deliver ozone to treating water.⁵² It also mentioned that the generated ozone gas can be supplied to the contact tank through nozzles at the bottom of the tank.⁷⁹

A compelling case study has been conducted very recently, focusing on the ten largest WWTPs in Sweden, to assess the feasibility of utilizing byproduct oxygen for wastewater ozonation, assuming that 50% of outgoing water must be ozonated. The study estimated the total use of oxygen for ozone generation while emphasizing that ozonation can be expected to be implemented at more and more WWTPs in the future.⁷⁹ Comparing ozone generation using air and pure oxygen, the gas stream produced from the air will possess ozone levels ranging from 0.5 to 3.0% by weight, while utilizing pure oxygen will result in a concentration roughly two to four times higher. Also, it has highlighted that if pure oxygen is employed as the input gas, the gases discharged from the contact chamber can be recycled for ozone generation or reused in the aeration tank.84 Moreover, the potential cost savings due to the lesser power consumption, minimum maintenance of the generators, compatibility with different

kinds of ozone generators, and flexible design are other significant advantages that can be achieved while using pure oxygen for ozone generation.

5.3 Utilizing H₂O₂ in wastewater treatment

5.3.1 Generating H_2O_2 using the by-product

oxygen

H₂O₂ is increasingly used in wastewater treatment because of its effectiveness in oxidizing pollutants, environmental friendliness, and potential for in-situ generation. Combining aerobic biological treatment and chemical oxidation utilizing hydrogen peroxide as the oxidant enables efficient control of the organic load, odour, and foaminess in household wastewater.⁸⁵ In brief, it comprises a comprehensive set of advantages, including oxidation of organic compounds, removal of inorganic compounds such as heavy metals, odour and colour removal, disinfection, and pH adjustment. More importantly, H₂O₂ is frequently utilized as an oxidizing agent in the Advanced Oxidation Processes (AOP) owing to its capacity to generate highly reactive hydroxyl radicals (•OH) and the synergistic application of hydrogen peroxide with additional methods, such as UV irradiation, significantly improves the overall efficiency of this process.

Even though the anthraquinone oxidation process (AO) is the most widely used H_2O_2 generation method, as it contributes to more than 95% of the total production every year, ⁸⁶ the AO process has several shortcomings that inspire the exploration of alternative synthesis methods.⁸⁷ The approaches for H_2O_2 synthesis can be categorized into four main groups: direct synthesis from hydrogen and oxygen, photo-catalysis, oxygen electroreduction, and water oxidation. The generation of H_2O_2 using 2-electron oxidation electroreduction is considered one of the most appealing alternatives with its applicability in terms of in-situ H_2O_2 generation at atmospheric pressure

and moderate temperature.⁸⁷ It has been highlighted that increased oxygen purity and elevated flow rates establish favourable conditions for H₂O₂ production⁸⁸⁻⁹¹, which can be further optimized for greater effectiveness by elevating oxygen utilization efficiency and reducing energy loss.⁸⁷ Accordingly, as the purity of oxygen can significantly impact the efficiency and the yield of the H_2O_2 generation, the by-product oxygen from green H₂ generation using the water electrolysis method can be effectively utilized in the H₂O₂ synthesis process while reducing the likelihood of contamination by the impurities. Further studies are encouraged to precisely determine the effectiveness of this high-purity oxygen in terms of H₂O₂ generation.

5.3.2 Co-production of H_2O_2 alongside green

hydrogen generation

Instead of generating oxygen as the by-product, the right electrocatalysts as the anode enable the generation of H₂O₂ via water oxidation.⁹² This has been experimented with using a hydrogen electrode equipped with platinum meshes, a hydrogen peroxide electrode featuring carbon material, and a Nafion electrolyte. A high efficiency was observed in the H_2O_2 generation process. Further, it was observed that the costs of this simultaneous generation are lower when compared with the conventional production techniques.⁹³ Considering the possibilities associated with the co-location of hydrogen generation and wastewater treatment industries, the on-site generation of H₂O₂ can avoid the high storage requirement of H₂O₂ while minimizing the risks associated with storing this hazardous chemical.

H₂O₂ co-electrosynthesis (at the anode) alongside hydrogen (at the cathode) happens via a 2electron water oxidation reaction (WOR). However, at the anode, the 2-electron WOR competes with a much more favourable 4-electron electrochemical pathway, the oxygen evolution reaction (OER), and 1-electron WOR, which produces OH radicals. The dominance of one pathway over the other can be influenced by various components within the water electrolysis system. Notably, boron-doped diamonds and carbon fibres have been identified as suitable catalysts for facilitating 2-electron WOR, while metal or alloy catalysts are more predisposed to catalysing OER. Additionally, the choice of electrolyte plays a crucial role in H_2O_2 production, and potassium bicarbonate emerges as a favourable option for promoting H_2O_2 generation.⁹⁴

 H_2O_2 is an effective agent in mitigating various wastewater concerns, including reducing BOD, COD, offensive odours, and foam formation in both domestic and industrial settings. Its versatile application extends to functioning as an independent treatment method or enhancing existing physical and biological treatment processes. H_2O_2 can be used alone or with a catalyst such as iron (Fe²⁺ or Fe³⁺), UV light, ozone catalytic autoxidation and the alkali.⁹⁵ These combinations are pivotal in reducing BOD/COD levels within wastewater.

In essence, by harnessing these co-products for wastewater treatment applications, we contribute to environmental stewardship and introduce a significant economic dimension to the green hydrogen production landscape.

5.4 On-site integration of wastewater treatment and electrolysis

Sector coupling in wastewater treatment for hydrogen production has recently drawn much focus, with further emphasis on utilizing surplus electricity in hydrogen generation where the coproduced oxygen can potentially enhance the treatment process of the wastewater treatment plant. ⁹⁶ It has been identified that the best techniques for co-located hydrogen production are those based on the electrolytic splitting of water.⁷⁶ Integration of water electrolysis-based hydrogen generation with wastewater treatment fosters prospects of self-sufficiency in renewable energy generation and utilisation and the ability to establish a potential income stream.⁷⁴

Notably, the areas with the greatest potential for renewable energy and having ample space for building green hydrogen plants are experiencing

an increasing concern regarding water stress.⁵ Therefore, using fresh water for green hydrogen generation is impractical and environmentally unsustainable, given the potential competition for limited freshwater resources and the associated environmental impacts in those areas. Interestingly, the regions where most wastewater treatment plants are situated tend to align with areas with significant renewable energy potential from wind and solar sources (See Figures 3-1 and **5-1**). Promoting co-location through the strategic placement of hydrogen generation facilities near wastewater treatment plants, coupled with the utilization of treated wastewater meeting the necessary quality standards for water electrolysis, emerges as a sustainable and promising approach. Effective integration of hydrogen production into wastewater facilities will reduce the energy demand for the waste treatment industry and support the synthesis of low-carbon fuel, aiding in the decarbonization of other sectors.⁷⁶



Figure 5-1 Predicted regional net present value for a large-scale hybrid wind and solar photovoltaicpowered hydrogen plant. Source: Geoscience Australia⁹⁷

In regions with consistently high-capacity factors, the costs associated with electricity generation decrease, leading to a reduction in the overall cost of hydrogen production, as depicted in **Figure 5-2**.⁹⁸ The presence of renewable energy sources differs greatly from one region to another,

influenced mainly by the natural productivity of wind and solar farms. Each area boasts unique solar and wind generation characteristics, which directly affect the practicality of hydrogen production and the associated expenses involved in its implementation.



Figure 5-2 Modelled cost of hydrogen production using solar photovoltaics or wind as electricity input. Source: International Energy Agency ⁹⁸

In line with earlier discussions, combining water electrolysis with wastewater treatment has multiple advantages. Some of them are enhanced recycling and utilization of treated wastewater in green hydrogen generation (minimum water transportation), the possibility of using high purity oxygen (HPO) in aerobic and disinfection processes, the capability to store energy onsite for subsequent or strategic usage within the WWTP and utilization of waste heat from the electrolyser to enhance the overall efficiency of the wastewater treatment process. Moreover, scaling up the use of renewable energy to power the WWTP for the transition towards achieving net-zero emissions and economic advantages derived from the production and sale of renewable hydrogen to local markets, facilitating the decarbonization of industries that are challenging to transform are some additional advantages of the co-location. In brief, integrating sustainable hydrogen production and wastewater treatment into a cohesive process makes aligning the renewable energy supply with the diurnal oxygen demand viable.74

Apart from the prospective benefits following the co-location, several important synergies drive the build-up of hydrogen and water treatment facilities

next to each other while making it a simplified and appealing procedure.

- Water treatment facilities are inherently situated near residential and industrial areas, where there will be future demand for hydrogen.
- The designation of land use for treatment facilities can be adapted to accommodate activities related to hydrogen production (smooth regulatory approval procedures).
- The availability of adequate land area for hydrogen plant installation (no additional cost for purchasing lands)⁷⁶

However, while the utilization of by-product oxygen is a benefit of co-location, it is crucial to identify a buyer or recipient for the primary hydrogen product by on-site use, direct supply to local users, supply to regional consumers through the grid, or as a third-party electrolyser operator that hosted at the water treatment facility. Also, special consideration should be given to the inherent collaborations that arise when wastewater volume increases in tandem with population density and industrial activity, such as utilizing hydrogen for public transportation or meeting the heat demand in different sectors.⁷⁶ If local transportation and industrial sectors shift toward hydrogen utilization, communities may enjoy heightened energy security and reduced air and noise pollution. Further, from a market perspective, co-locating hydrogen production has the potential to generate local employment opportunities.

Moreover, a substantial potential exists for highly efficient system integration of more industrial opportunities near WWTPs. This integration involves merging hydrogen production with current industrial supply chains, such as ammonia and alumina production, presenting a promising outlook. Some WWTPs are strategically positioned near existing ammonia production facilities, exemplified by the Kwinana and Newcastle ammonia plants. Over the long term, the on-site strategy, in synergy with Australia's competitive advantage in alumina production, could unlock additional opportunities for sustainable growth.⁷²

Producing green hydrogen by integrating wind or solar energy with an electrolyser requires carefully considering the balance between installed renewable energy and electrolysis capacity. This balance directly impacts the average utilization rate of the electrolyser. For instance, in a scenario where a 1 MW electrolyser system is in place, pairing it with 1 MW of installed wind capacity would typically provide an average output of 400 kW, based on a 40% average capacity factor.99 The utilization rate of the electrolyser aligns with the capacity factor of the wind. Increasing the electrolyser's utilization rate and reducing its levelized cost requires installing more wind capacity. However, this increase must be managed alongside the wind output curve, which may result in an oversupply of electricity at certain times of the year. This surplus electricity can be exported if connections are available, or it can be utilized onsite. Otherwise, it may go to waste. Therefore, a balance must be struck between optimizing electrolyser utilization to lower costs and potentially incurring increased costs due to unused wind capacity. This trade-off is crucial in ensuring efficient and cost-effective green hydrogen production.¹²

Establishing well-informed policies is also crucial for co-location due to the uneven distribution of tertiary water effluent sources across Australia, particularly close to major urban areas in most states. It is further recommended to pay greater attention to 'Hydrogen Hubs'- locations where hydrogen plants are situated near hydrogen exporting facilities- in terms of their water access requirements and the potential for co-location with water resources.⁵

Chapter 6. Outlook and Recommendations

WWTPs are in a unique position of competitive advantage regarding the requirements of green hydrogen production, including having access to water, land away from population centres but close to markets, and renewable energy. The evolution of water electrolysis has led to the emergence of four main technologies, each based on different types of electrolysers. Beyond the This section provides outlooks and recommendations for integrating electrolysis into green hydrogen and chemical co-production, such as H₂O₂, ozone, and oxygen, alongside wastewater treatment. Collaborative efforts between urban water management professionals and governmental bodies are expected to leverage their expertise to ensure sustainable water provision, balancing environmental responsibility,

generation of green hydrogen, the beneficial byproducts resulting from the anode are efficiently transported back to the water treatment plants, ultimately achieving a circular economic model. As presented in Chapter 4, there is a clear gap in water quality between WWTP effluents and electrolysis requirements.

cost-efficiency, and community expectations. The recommendations are categorised broadly into three (**Figure 6-1**): (1) recommendations on the design of the water electrolysis system, (2) recommendations on the wastewater treatment upgrade at WWTPs, and (3) recommendations on the integration of water electrolysis and existing WWTPs.



Figure 6-1 Summary of the recommendations citing the gap between WWTPs effluents and water electrolysis.

6.1 Recommendations on water electrolysis system

Designing a hydrogen electrolyser for utilizing lowquality water, such as treated water from WWTPs, requires careful consideration of its components, especially the catalyst, membrane, and electrode, to ensure efficiency, durability, and costeffectiveness. Here are some recommendations:

Catalyst:

Select Robust Catalysts for OER and HER: Choose materials that show high activity and stability in the presence of impurities typical of low-quality water. Nickel-iron (NiFe) oxyhydroxide for OER and transition metal sulphides/phosphides/nitrides for hydrogen evolution reaction HER have shown promising resistance to chloride-induced corrosion and high selectivity in challenging conditions.

Optimize Catalyst Surface: Implement surface engineering techniques, such as doping and vacancy engineering, to enhance the catalyst's tolerance to impurities and improve its activity. These modifications can also help reduce the impact of precipitate formation from calcium and magnesium ions.

Membrane:

Choose Resistant Membrane Materials: Opt for membrane materials that can withstand the chemical and physical stresses induced by lowquality feed water. AEMs may offer better resistance to fouling and degradation compared to PEMs in certain impure water conditions.

Incorporate Fouling Resistance: Design membranes with anti-fouling coatings or structures to minimize the impact of biofouling, scaling, and other forms of clogging, ensuring consistent water flow and ion exchange. Design for Durability: Electrodes should be made from materials that resist corrosion and fouling in the presence of impurities. Using advanced alloys or coatings can protect electrode surfaces from degradation, extending the electrolyser's operational lifespan.

Adapt Electrode Structure for Efficiency: The electrode structure should maximize the active surface area and facilitate efficient gas release. This can be achieved by using porous materials, nanostructuring, or incorporating flow channels that enhance mass transport and reduce concentration polarization.

General Design Considerations:

Implement Pre-treatment Strategies: Although focusing on the resilience of internal components is crucial, integrating effective pre-treatment of feed water to remove most contaminants before electrolysis can significantly reduce the burden on the electrolyser components.

Modular and Scalable Design: Consider modular designs that allow for easy replacement or scaling of components based on water quality and production needs. This flexibility can accommodate variations in water quality and demand.

Continuous Monitoring and Maintenance: Incorporate sensors and monitoring systems to track performance and identify issues related to impurity build-up, enabling timely maintenance or component replacement.

6.2 Recommendations on WWTPs upgrade for Hydrogen Economy

Australia's array of WWTPs exhibits a range of water quality outcomes due to varied treatment processes. At the same time, some incorporate tertiary treatment, while others do not, creating discrepancies in the suitability of the effluent for

Electrode:

use in hydrogen production. The stringent water quality requirements of electrolysers necessitate that effluent, even post-tertiary treatment, often requires additional purification. Infrastructure upgrades are imperative to align existing WWTPs with the rigorous demands of hydrogen electrolysis. Recommendations for these upgrades include:

In-depth Analysis of Impurities: Gain a thorough understanding of the specific impurities present in wastewater and how they affect the long-term performance of electrolysers. This knowledge is vital for targeting the removal of the most detrimental contaminants.

Reverse Osmosis (RO) Systems: Install RO systems to reduce the dissolved solids in the wastewater if tertiary treatment does not exist, achieving the high purity levels essential for the electrolysis process. Employ microfiltration or ultrafiltration to eliminate fine particulates, safeguarding subsequent processes like reverse osmosis from blockages and efficiency losses.

Ion Exchange Techniques: Ion exchange systems might be needed to remove specific ions harmful to electrolysis, such as calcium, magnesium, and certain heavy metals, enhancing the suitability of the treated water.

Advanced Oxidation Technologies (AOTs):

Incorporate AOTs, like UV/hydrogen peroxide or ozone treatment, to decompose stubborn organic compounds if their concentration is still too high after secondary treatment, lower COD, and manage microbial populations, preparing the water for electrolytic hydrogen production.

6.3 Recommendations on the integration of water electrolysis and existing WWTPs

Integrating wastewater treatment with green hydrogen production presents a significant opportunity to enhance sustainability and resource optimization in Australia. Here are five strategic recommendations to consider for this integration:

Cross-Industry Integration: Foster a symbiotic relationship between wastewater treatment and hydrogen production sectors. By leveraging the by-products of electrolysis, such as oxygen, hydrogen peroxide, and ozone, the efficiency of WWTPs can be improved, contributing to economic and environmental sustainability. The use of by-products like hydrogen peroxide for disinfection in WWTPs could potentially be realized by adapting electrolyser technology.

On-Site Treatment and Electrolysis (Co-location Strategies): Implement on-site wastewater treatment coupled with hydrogen electrolysis. Colocation can minimize water transportation, enhance energy and heat recovery, and capitalize on the economic benefits of local renewable hydrogen markets, propelling both sectors towards greater sustainability and economic efficiency.

Sector Coupling: Harness surplus electricity for hydrogen generation, where the oxygen byproduct can be utilized to improve wastewater treatment processes. This approach promotes the use of renewable energy within the WWTPs and could create additional revenue streams from hydrogen sales. *Feasibility Studies:* Undertake detailed studies to evaluate the practicality and economics of using electrolysis by-products in WWTP processes. Understanding the cost implications and potential savings is crucial for informed decision-making and investment in the technology.

Policy Development: Develop supportive policies that encourage the co-location of hydrogen production and wastewater treatment operations. Policies should account for the distribution of tertiary-treated effluent and the establishment of 'Hydrogen Hubs', maximizing the use of local water resources and aligning with broader environmental goals.

By considering these recommendations, Australia can create a synergistic approach between wastewater management and hydrogen production, leading to advancements in water conservation, energy efficiency, and a stronger, greener economy.

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Afterword

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Appendix

	AWE	PEMWE	AEMWE	SOEC
Operating temperature (°C)	70-90	50-80	40-60	700-850
Operating pressure (bar)	1-30	< 70	< 35	1
Electrolyte	Potassium hydroxide (KOH)	PFSA membranes (Solid	Divinylbenzene (DVB) support	Yttria-stabilized Zirconia (YSZ)
	5-7 molL ⁻¹	electrolyte)	with KOH or NaHCO3 1molL ⁻¹	
Separator (diaphragm)	ZrO ₂ stabilized with PPS mesh	PFSA membranes	Divinylbenzene (DVB) support	Yttria-stabilized Zirconia (YSZ)
			with KOH or NaHCO3	(Solid electrolyte)
			(Solid electrolyte)	
Cathode catalyst	Nickel-coated perforated	Platinum nanoparticles on	High surface area nickel	Ni/YSZ
	stainless steel	carbon black		
Anode catalyst	Nickel-coated perforated	Iridium oxide	High surface area Nickel or	Perovskite-type
	stainless steel		NiFeCo alloys	
Cathode substrate	Nickel mesh	Sintered porous titanium or	Nickel foam or carbon cloth	N/A
		carbon cloth		
Anode substrate	Nickel mesh	Platinum-coated sintered	Nickel foam	Coarse Nickel-mesh or foam
		porous titanium		

 Table 2-1 Conditions for the different types of typical water electrolysers.

 Table 2-2 Major manufacturers of water electrolysers

AWE	PEMWE	SOEC	AEMWE
AquaHydrex (Australia)	Cummins (US)	Ceres (UK)	Enapter (Italy)
Tianjin Mainland (China)	Elogen (Germany)	Haldor Tøpsoe (Denmark)	
LONGi (China)	ITM Power (UK)	Sunfire (Germany)	
Asahi Kesei (Japan)	NEL Hydrogen (Norway)	Toshiba (Japan)	
John Cockerill (France/Belgium)	Siemens Energy (Germany)		
McPhy (France)	Plug Power (US)		
Teledyne (US)			
Cummins (US)			
NEL Hydrogen (Norway)			
Thyssenkrupp Uhde (Germany)			

 Table 2-3
 Scalability of production processes

Manufacturer	Technology Name	Operating Pressure	Hydrogen Flowrate	Energy Consumption	Operating Range	Water Consumption	Power	Electrical Efficiency	Current Density
Proton Onsite	HOGEN S10		0.265 Nm ³ /hr - 0.57kg/d	74 kWh/kg H ₂	0-100%	9.9 L/kg H ₂	1.1 kW	-	 Purity: 99.9995% (Water vapour < 5 ppm, N2 < 2 ppm, O₂ < 1 ppm)
	HOGEN S20	13.8 bar _g	0.53 Nm ³ /hr - 1.14 kg/d				2.2 kW	-	• Air-cooled with ambient air
	HOGEN S40		1.05 Nm ³ /hr - 2.27 kg/d				4.3 kW	-	maximum heat load of 1.1 kW, 2.2 kW and 4.3 kW
	H2		2 Nm ³ /hr	81 kWh/kg H ₂	0-100%	10.2 L/kg H ₂	8.1 kW	-	 Purity: 99.9995% (Water vapour < 5 ppm, N2 < 2ppm, O2 < 1 ppm)
	H4	15 bar _g / 30 bar _g	4 Nm ³ /hr	78 kWh/kg H ₂			16.1 kW	-	 Liquid cooled with water at a
	H6	option	6 Nm ³ /hr	76 kWh/kg H ₂			23.7 kW	-	temperature not exceeding 25°C, with a maximum heat load of 8.1 kW, 16.1 kW and 23.7 kW
H-TEC	ME 100/350	15 - 30 bar _g	15-46.3 Nm ³ /hr	55 kWh/kg H ₂	32-100%	14.4 L/kg H ₂	225 kW	73%	-
Systems	ME 450/1400	15 - 30 bar _g 42-210 Nm ³ /hr		53 kWh/kg H ₂	20-100%	13.8 L/kg H ₂	1 MW	74%	-

	HCS 2MW	15 - 30 bar _g	420 Nm ³ /hr	<53 kWh/kg		16 L/kg H ₂	2 MW		-	
	HCS 4MW	15 - 30 bar _g	840 Nm ³ /hr	<53 kWh/kg H ₂	20-100%	17 L/kg H ₂	4MW	>74%	-	
	HCS 10MW	15 - 30 bar _g	2100 Nm ³ /hr			18 L/kg H ₂	10MW		-	
	S30/10	0 - 20 bar _g	0.22 Nm ³ /hr	-	-	29 kg/hr	1 kW		 Flowrate of cooling water 29 kg/hr 	
	S30/30	0 - 20 bar _g	0.66 Nm ³ /hr		-	87 kg/hr	3 kW	78%	 Flowrate of cooling water 87 kg/hr 	
	S30/50	0 - 20 bar _g	1.10 Nm ³ /hr	-	-	145 kg/hr	5 kW		 Flowrate of cooling water 145 kg/hr 	
	HyLYZER 200		200 Nm ³ /hr	<55 kWh/kg						
Hydrogenics	HyLYZER 250	30 bar	250 Nm ³ /hr	H ₂	5 - 100%	9 L/kg H₂	-	-	• Purity: 99.998% (O2 < 2 ppm, N2	
	HyLYZER 400	9	400 Nm ³ /hr	<54 kWh/kg H ₂					< 12 ppm)	
	HyLYZER 500		500 Nm ³ /hr							

	HyLYZER 1000		1000 Nm ³ /hr	<51 kWh/kg H ₂	5 - 125%				 Purity: 99.99% dry basis, gas is fully saturated with water and O2 < 100 ppm Optional > 99.998% with hydrogen purification system Cooled with water
Siemens	SILYZER 200	35 bar	225 Nm ³ /h	-	-	17 L/kg H ₂	1.25 MW	60-65%	 Purity: 99.5 - 99.9% but has DeOxo/Dryer option to reach Quality 5.0 Purity: 99.999%
NEL	M-Series	- 30 bar _g	1300 kg/hr 1700-4900 Nm3 /hr	- 4.5 kWh/Nm3	0-100% 10 - 100%	-	~70 MW 7.7 - 22 MW	-	 Purity: 99.999% Purity: 99.9995% (O2 < 1 ppm, H₂O < 5 ppm)

Table 2-4 Simulated water treatmen	costs for supplying	water electrolysis (\$/m ³) ³⁹
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Water sources	Coast area		Rural area			
	CAPEX	OPEX	CAPEX	OPEX		
Industrial water	3.038	2.975	4.968	3.005		
Urban water	3.343	2.975	3.750	3.005		
Seawater	7.747	6.972	N/A	N/A		
Cooling water	2.737	2.860	N/A	N/A		
Rainwater	4.655	0.733	4.655	0.765		
Surface water	1.427	2.922	3.255	2.950		
Groundwater	3.180	2.998	3.180	3.027		

 Table 3-1 The function of each treatment process in reducing the specific contaminants.

Contaminants	TSS	TDS	BOD	COD	тос	TN	ТР	ions
Treatments								
Preliminary	\checkmark							
Primary	\checkmark	\checkmark	\checkmark					
Secondary	\checkmark		\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	
Tertiary (Membrane)	\checkmark							

	Beenyup	AWRP (Ter	tiary	Aurora R	WTP		Western Treatment Plant			Pakenham Water Recycling			
Con.	effluent)			(Class A	(Class A effluent)			(Class A effluent)			Plant (Secondary effluent)		
mg.L ⁻¹	2021	2022	2023	2020	2021	2022	2020	2021	2022	2020	2021	2022	
Ammonia	<0.9	<0.9	<0.9	0.979	0.028	0.01	0.7	<0.1	0.3	0.7	0.2	2.1	
Na ⁺	8.4	7.3	8.7	102	110	117	220	250	300				
K ⁺				19.4	20.3	16.5							
Ca ²⁺	< 0.1	< 0.1	< 0.1	18.2	22.2	20.4	30	28	30				
Mg ²⁺	<0.1	< 0.1	<0.1	47.5	66.5	101	24	25		11			
Al ³⁺	<5×10 ⁻³	<5×10 ⁻³	<5×10 ⁻³				0.02	0.05	0.04	0.09	0.01	0.01	
Cr ³⁺	<10-3	<10 ⁻³	<10 ⁻³				<10-3	<10 ⁻³	<10-3				
Cd ²⁺	<10-4	<10-4	<10-4				<2×10 ⁻⁴	<2×10 ⁻⁴	<2×10 ⁻⁴	<2×10 ⁻⁴	<2×10 ⁻⁴		
Co ²⁺	<10-4	<10-4	<10-4				<10-3	<10-3	<10-3	<10-3	<10-3		
Cu ²⁺	6×10 ⁻⁴	<10-4	<10-4				0.003	0.004	0.006	0.003	0.002	0.002	
Fe ³⁺	<5×10 ⁻³	<5×10 ⁻³	<5×10 ⁻³				< 0.01	0.07	0.08	0.14	0.03		
Mn ²⁺	<10-3	<10-3	<10-3				0.12	0.03	0.1	0.008	0.002		
Ni ²⁺	<10-3	<10-3	<10-3							0.002	0.002		
Zn ²⁺	<5×10 ⁻³	6×10 ⁻³	<5×10 ⁻³				0.021	0.02	0.014	0.01	0.001		
Pb ²⁺	<10-4	<10-4	<10-4				<10-3	<10-3	<10-3	<10-3	<10-3	<10-3	
SO4 ²⁻	<0.1	<0.1	<0.1								39	34	
PO4 ³⁻			<5×10 ⁻³										
Cl-	5	5	6	114		118	460	390	410		120	120	
HCO3 ⁻	11	8	8	280	409	520							

 Table 3-2 Historical water quality data of WWTPs in Australia (Source: Water RA).

Dissolve oxygen			8.7									
Conductivity (µS/cm)			20-150	976	1180	1240	1600	1700	1800	740	700	883
рН	6.8-7.5	6.9-7.5	6.9-7.5	7.6	7.7	7.8	7.4	7.8	7.9			
Suspended solids	<1	<1	<1	<1	<1	<1	<2	<2	<2	<2	<2	<2
Total dissolved solids	10-42	26-46	20-40	508	655	689						
Total organic carbon	<10 ⁻³	<10-3	<10-3							5	6.7	7.5
Hardness (CaCO ₃)	9	7	6	241								
Table 3-3 Summary of tertiary water effluents across WWTPs of Sydney Water.

Sydney Water WTPs	Amount of tertiary water effluent	Unused tertiary water effluent	
	(ML/day)	(ML/day)	
Rosehill - Camelia	24.2	-	
Rouse Hill	24	-	
Wollongong S1	22	2	
Quakers Hill	16	14.5	
West Camden	15	10	
Liverpool	9	3.6	
Castle Hill	5	3	
Hoxton Park	4	-	
Picton	3	0.8	
Richmond	2.8	-	
Gerrigong Gerroa	2.2	2.2	
Wollongong S2	2	-	
St Marys	1.5	1	
Penrith	1	0.5	
Bombo	0.7	-	
TOTAL	132.4	37.6	

 Table 4-1 Impact of impurities on AWEs and AEMWEs

Impurity	Source	Impact on Anode	Impact on	Impact on Cathode	
type			Separator/membrane		
Fe ³⁺	Electrolyte	Adsorbs on the catalyst. Improvement of		Improvement of HER activity depends on	
	impurity	OER activity depends on concentration.		concentration.	
Ni ²⁺	Electrolyte	Adsorbs on the catalyst. Improvement of		Improvement of HER activity	
	impurity	OER activity			
Al ³⁺	Electrolyte	Adsorbs on the catalyst. No adverse effects		No adverse effects were reported.	
	impurity	were reported.			
Zn ²⁺	Gasket leaching	Catalyst poison		Forms dendrites at negative potentials,	
	out, electrolyte			catalyst poison	
	impurity				
Cd ²⁺ ,	External	Catalyst poison			
Pb ²⁺	contamination				
Ti ³⁺ /Ti ⁴⁺	Electrode			Improvement of HER activity	
	leaching out				
Na+	Water impurity	No adverse effects reported		No adverse effects were reported.	
	(if NaOH is not				
	used)				
Ca ²⁺ ,	Water impurity	Deposits of Mg(OH) ₂ at high pH may cause mass transport issues at electrodes.			
Mg ²⁺					
Cl-	Water impurity	Nickel corrosion, apart from special			
		structures.			

CO ₂	Air		Lowers conductivity, reduces	Increases charge transfer resistance (AEMWE)
	contamination		side chain spacing and	
			membrane crystallinity	
Organics	Water impurity	Catalyst poison		Catalyst poison
				
Inert	Precipitates		Clogging of pores	
impurities	formed by			
	reaction with			
	electrolyte			

 Table 4-2 Impact of impurities on PEMWE components.

Impurity	Source	Cell components	Membrane	Anode	Cathode
Na ⁺ , Mg ²⁺ ,	Seawater, potable water		Lowers membrane	Lowers ionomer	Lowers ionomer
Ca ²⁺			conductivity	conductivity, catalyst poison	conductivity, decreases the rate of
					HER
Ti ⁴⁺	PTL corrosion				
Ni ²⁺ , Cu ²⁺	External contamination				
Fe ²⁺ , Fe ³⁺	Stainless steel tubing		Lowers membrane		
	degradation		conductivity, degrades		
			membrane		
Ir ⁿ⁺	Anode catalyst dissolution				
Cl-	Water purification failure			Enhances dissolution, catalyst poison, unwanted side product	
F-	Water purification failure,	Corrodes Ti PTL		Enhances dissolution	
	membrane degradation	and BPP			
Br [_] , I [_]	Water purification failure			Enhances dissolution, catalyst poison	
SO4 ²⁻	Water purification failure,			Catalyst poison	
	membrane degradation				
Organics	External contamination			Enhances dissolution, catalyst poison, unwanted side product	
Solid	External contamination			Blocks PTL pores and induces	
particulates				mass transport issues	