

Singapore International Water Week April 2022:

# Hydrogen Circular Economy: Viability, Scalability, & Risk For Water Industry

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# Introduction

Integration of sustainable hydrogen (H<sub>2</sub>) production with capture of associated greenhouse gases & carbon, & local use of co-products:

- facilitate an emerging circular economy,
- help the water industry to achieve net zero carbon emissions,
- supply chain security for water treatment chemicals.

In particular, green hydrogen & co-products such as O<sub>2</sub>, O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> are essential within an emerging circular economy:

- sustainable fuels,
- chemical synthesis feedstocks,
- oxidising agents for AOP.



# Introduction

Wastewater treatment plants produce large quantities of recycled water & biogas, providing co-location opportunities for hydrogen production and alternative reuse prospects:

- Water source concerns for sustainable hydrogen,
- Reinforces circular economy principles of wastewater as a valuable resource,
- Avoids potentially harmful wastewater discharges to the environment,
- Reduces capital expenses by using existing infrastructure, land, & supply chains.
- + recycled-water-based drought schemes may have potential for hydrogen production during non-drought periods.

# Challenge

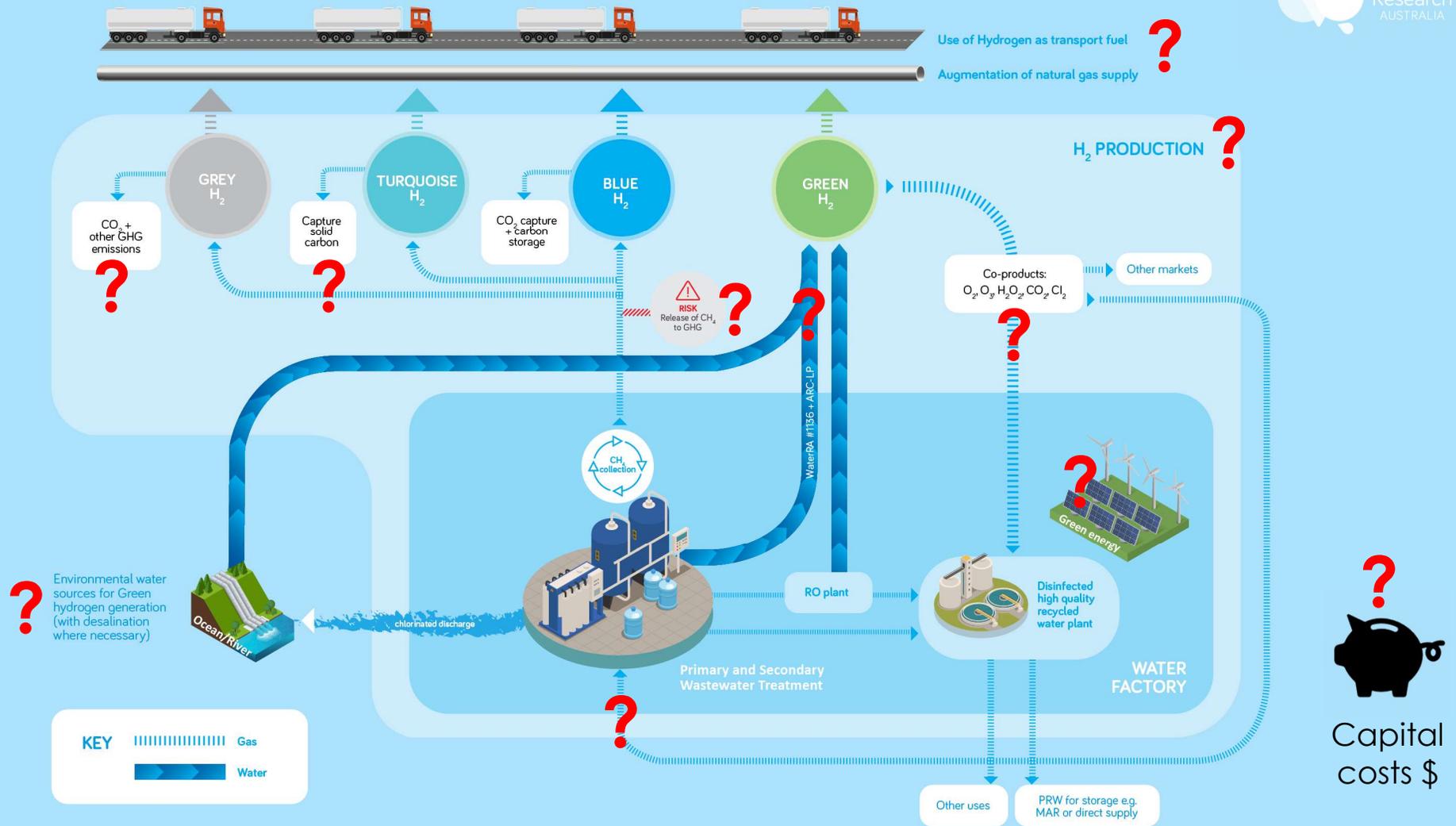
While hydrogen production opportunities may add significant value to WWTP operations:

- Associated risks
- Viability?
- Scalability?
- Urban and regional perspectives?
- Value proposition of a hydrogen circular economy to water industry stakeholders?

# Objective

- Understand these concerns and provide site-specific guidance to prospective utilities aiming to address technical considerations of feasibility, scalability and viability
- Formulate a decision tree to support utility decision-making and risk assessment.

# Conceptual model of how the water industry can drive a circular economy



# Economic viability

Understand the economic viability of hydrogen production:

- Projected future demands for hydrogen & associated supply chain
  - The global hydrogen industry is expected to increase 40% by 2030, with Australia aiming to become a leading exporter of hydrogen, with potential export values of \$5.7bn by 2040.
  - To accelerate the development of a hydrogen economy and transition to a decarbonised future, we need to produce “clean” hydrogen at under AU\$2.00 per kilogram.



# Economic viability

Understand the economic viability of hydrogen co-products:

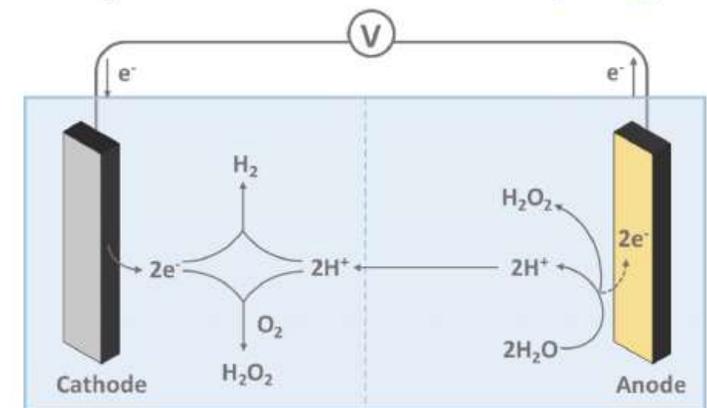
- Projected future demands for co-products: O<sub>3</sub>
  - The global O<sub>3</sub> market size was valued at USD \$ 880 million in 2016 and is expected to grow at a compound annual growth rate (CAGR) of 7.4% from 2017 to 2023.
  - O<sub>3</sub> generators predominantly use air as the feed, but when oxygen is used, more ozone can be generated at lower energy consumption.
- Projected future demands for co-products: H<sub>2</sub>O<sub>2</sub>
  - Use in water industry; food, paper and pulp; chemical manufacturing; pharmaceutical & health; disinfectant products.
  - The global hydrogen peroxide market size was valued at USD 1.44 billion in 2020 and is expected to grow at a compound annual growth rate (CAGR) of 5.7% from 2020 to 2028.
    - *Can production of co-products offset the production cost of H<sub>2</sub>, bringing the cost of H<sub>2</sub> production down to the targeted \$2/kg?*

# Technical viability

The technical viability of recycled-water-based hydrogen production also presents many research questions:

- Performance of electrolysers (which split water into hydrogen and oxygen in the presence of a catalyst)
  - low pH conditions ideal for hydrogen reduction
- Volumes of (recycled) water required
- Optimal operating conditions
- Impacts of contaminants in wastewater:
  - organic compounds
  - metal ions
  - nutrients
  - inorganic debris

Principles of electrochemical water splitting



# Technical viability: WaterRA factsheet

[https://www.waterra.com.au/r11390/media/system/attrib/file/2690/WaterRA\\_FS\\_1136\\_HydrogenEconomy.pdf](https://www.waterra.com.au/r11390/media/system/attrib/file/2690/WaterRA_FS_1136_HydrogenEconomy.pdf)



### Background

Excess electrical energy generated by renewable sources including photovoltaic systems during daylight hours could be used to power electrochemical water splitting to produce hydrogen (H<sub>2</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), both of which are essential chemicals for the emerging hydrogen economy as fuels, feedstocks in chemical synthesis, or oxidising agents in advanced oxidation processes. Water splitting traditionally uses freshwater, which is already a scarce resource in many countries including Australia. Additional consumption of freshwater for this purpose will increase operational costs of production and place additional stress on water resources. In major Australian urban areas, large volumes of recycled wastewater (RWw) are generated by centralised municipal wastewater treatment plants (MWWTPs), which could provide a valuable alternative water source for future electrolysis. A potential drawback emerges when considering the potentially undesirable side effects of residual contaminants within RWw, which may reduce H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> production efficiencies and reduce electrolyser lifespan. The required water quality for this process is thereby informed by the key impurities that impede electrochemical H<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> production using RWw, establishing guidelines for electrolyser design and MWWTP operations and improvements.



### Key points:

- Solar-powered electrocatalytic H<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> production using recycled water can help to alleviate stresses on freshwater resources.
- Recycled wastewater contains key impurities which affect electrochemical processes and electrocatalyst lifespan.
- Existing gaps include a comprehensive review of the required quality of recycled wastewater for H<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> production by considering contaminants such as metal ions and organic compounds which persist after treatment processes.
- Addressing these gaps is necessary for the development of guidelines for electrolyser design and recycled wastewater treatment plant.

### Principles of electrochemical water splitting

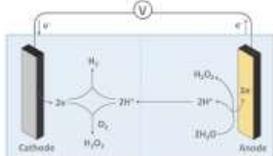
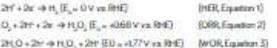


Figure 1. Schematic of the electrochemical water splitting process for H<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> generation.

Hydrogen is an attractive energy carrier due to its high energy density and lack of polluting by-products. Hydrogen produced via water splitting (Equation 1) can be stored, transported, then utilised as an energy source to restore a carbon-neutral cycle. Another attractive product of water splitting is hydrogen peroxide (Equation 2 and 3) which can be utilised as a sustainable oxidant reagent within advanced oxidation processes or as an energy source for local cells. By connecting the electrodes with a renewable power source in series, H<sub>2</sub> is produced by hydrogen reduction at the cathode (H<sub>2</sub>R, Equation 2) while H<sub>2</sub>O<sub>2</sub> is simultaneously generated either from oxygen reduction reactions (ORR, Equation 2) at the cathode

or water oxidation reactions (WOR, Equation 3) at the anode [1]. In acidic proton exchange membrane electrolysers (Figure 1), the generated protons at the anode are transported through a proton exchange membrane (PEM) to satisfy the electrochemical half-reactions at the cathode. To drive H<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> evolution, a minimum theoretical voltage for electrochemical water splitting is required to "overdrive" the energy levels of hydrogen reduction and water oxidation [2]. In practical electrochemical processes, an additional low voltage (overpotential) is also needed to drive the charge transfer process at the electrocatalytic interfaces, which reduces efficiency and increases energy consumption. Recent efforts have attempted to address this through extensive studies of low-cost electrocatalysts for efficient energy carrier production [3, 4]. For PEM-water electrolysis, enhancing the stability of electrodes and proton exchange membranes is also critical to implementing the process for long-term and large-scale uses [5].



### Impacts of electrolytes

Electrolyte ions impact on reaction kinetics and electrode stability by participating in electrochemical water processes and influencing mass transfer rates [6]. While conventional electrolytes work best within a high or low pH range (pH 13-14 or 0-1 respectively) at which sufficient concentrations of charge carriers can facilitate energy conversion reactions, there remains a mismatch between optimal conditions for HER (pH = 7) and WOR (pH = 7) [7]. A vast majority of electrocatalysts also tend to degrade at extreme pH values, which places constraints on the long-term stability of electrolysers. Near neutral pH values could avoid the potential degradation issues introduced by acidic electrolytes, alongside efforts to develop corrosion-resistant materials electrocatalysts with wider pH operating ranges are being investigated.

In addition to the influence of pH, soluble ions and molecules in electrolytes have been reported to have significant impacts on the efficiency of electrochemical reactions. The electrocatalytic layers of electrolysers have a porous structure. HER, ORR and WOR reactions

can only occur at the spatially confined sites around the interfaces between the catalyst layers and the proton membrane, called triple phase boundaries (TPBs), where both reactants and electrocatalytically connected catalysts contact. The reaction rates of electrochemical reactions highly depend on the properties of TPBs and the proton transport ability of PEMs. Previous studies have already shown that electrocatalysts and membranes in electrolysers are susceptible to feed-water impurities, particularly cations including Na<sup>+</sup>, Ca<sup>2+</sup> and Fe<sup>3+</sup> [8, 9]. While the mechanism of the metallic cation poisoning has not yet been fully understood, it is generally believed that these cations can occupy ion exchange sites in proton membranes and the cations in catalyst layers, reducing the proton mobility and increasing the overpotential of cathodes and anodes. The activity sites of electrocatalysts can also be blocked by organics and other impurities (see deposits within interconnected catalyst layer pores, decreasing the intrinsic reactivity of the electrocatalysts). Further efforts will be required to identify worst-case concentrations of feed-water impurities are tolerable in long-term operation electrolyser operations.

### Quality of recycled water

Table 1. Classes of recycled water and corresponding standards for biological treatment and pathogen reduction [10].

Water quality parameter	Class A	Class B	Class C
Turbidity	NTU	< 2	-
pH	-	6-9 <sup>a</sup>	5-9 <sup>b</sup>
Biochemical oxygen demand (BOD)	mg/L	10	20
Suspended solids (SS)	mg/L	5	30
Residual chlorine	mg/L	1	-
E. coli	org/100 mL	< 10 E. coli	100 E. coli

Use of RWw from MWWTPs presents as a potential solution to the high volume of water required for electrochemical H<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> evolution, as the Australian Guidelines for Water Recycling, recycled water is defined as water that has been treated to fit-for-purpose standards for specific applications [10]. The Environmental Protection Authority (EPA) provides threshold values of physical-chemical water quality (for example turbidity and BOD) and E. coli limits for biological treatment and pathogen reduction (Table 1) [10]. While the majority of pollutants in wastewater are effectively removed in the current wastewater treatment processes, small amounts of contaminants (e.g. metal ions, organic components, nutrients, etc.) remain in RWw [10]. This wide range of potential impurities introduces a need to assess the feasibility of RWw as an electrocatalytic medium, which first requires the identification of key impurities in recycled water and the threshold concentrations at which interferences in electrocatalytic processes can be anticipated.

### Summary

Electrolytic systems powered by renewable energy for the production of H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> may assist the development of sustainable water treatment processes and efficient utilisation of access energy. Beyond studies into active and robust electrocatalysts, the operation of electrochemical water splitting using RWw would provide an additional breakthrough for the translation of this technology into practical application. The identification of key impurities in RWw and an assessment on their impacts on electrochemical processes are necessary to assess the feasibility of utilising recycled water for electrochemical water splitting. Combining the types and concentrations of key contaminants in recycled water with threshold values for electrocatalysis will inform guidelines on electrolyser designs and operation, which will include how existing MWWTPs can be upgraded to facilitate energy efficient utilisation of H<sub>2</sub>O<sub>2</sub> in advanced oxidation processes for water treatment.

**Acknowledgment** - WaterRA Project 1136 team: Yue Lu, Liang Zhang & See Seung (Monash University) lead; Tullio Sforzini (Water Corporation), Li Gan (South East Water), Antoine Bredin (Yarra Valley Water), Mark Crislaru (Melbourne Water), Liam Vreugden & Anish Danyal (WaterRA).

### References

[1] H<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, 2024, 1 Jul, 23 Feb, Melbourne, 0 (2024) 9000 (2024)  
 [2] L. H. Wang, S. S. Sun, S. Wang, ChemSusChem, 10 (2017) 940-948.  
 [3] L. H. Wang, S. S. Sun, S. Wang, ChemSusChem, 10 (2017) 940-948.  
 [4] L. H. Wang, S. S. Sun, S. Wang, ChemSusChem, 10 (2017) 940-948.  
 [5] L. H. Wang, S. S. Sun, S. Wang, ChemSusChem, 10 (2017) 940-948.  
 [6] L. H. Wang, S. S. Sun, S. Wang, ChemSusChem, 10 (2017) 940-948.  
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 [10] Guidelines for Water Recycling: Pathways, Health and Environmental Risk, 2018.



# Technical viability

## 3-year ARC linkage project: Sustainable Hydrogen Production from Used Water

### Objectives

1. To gain an in-depth understanding of how existing electrolysers perform in the presence of water impurities, and develop guidelines for designing water electrolysers with high tolerance of water
2. To identify the water quality gap between the treated water from existing WWTPs and the required feed water for water electrolysis, and provide recommendations for WWTPs operation and potential upgrading;
3. To evaluate the technical feasibility of utilising the co-products from waster electrolysis in wastewater treatment, and develop frameworks for the integration between wastewater treatment and water electrolysis.

### Project partners & funding model



WaterRA water industry consortium:



Energy sector:  
Leverage 1\$:6\$



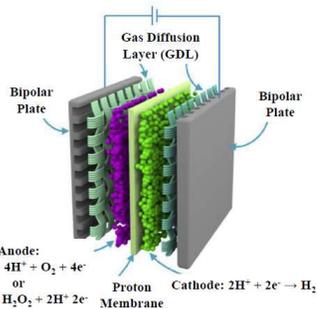
Academic research:



Academic research:  
Leverage 1\$:11\$



Australian Government  
Australian Research Council



## Technical viability: *Impacts of impurities & mitigation strategies*

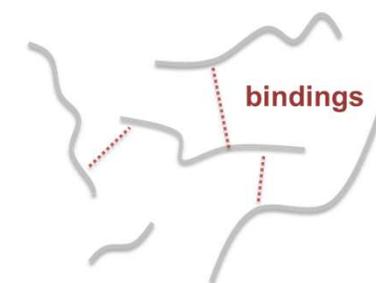
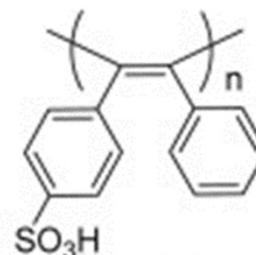
	TYPES	MECHANISMS	PERFORMANCE
Failure of exchange membranes	<ul style="list-style-type: none"> <li>Mechanical damage, e.g. cracks, pores</li> <li>Membrane degradation</li> <li>Active site occupation</li> </ul>	<ul style="list-style-type: none"> <li><math>\text{O}_2</math> permeation</li> <li>Low conductivity</li> </ul>	Activity decay
Electrode catalyst damage	<ul style="list-style-type: none"> <li>Dissolution/corrosion of catalysts</li> <li>Poisoned by impurities</li> <li>Agglomeration of catalysts</li> <li>Passivation of catalysts/supports</li> </ul>	<ul style="list-style-type: none"> <li>Changes in chemical/structural features</li> </ul>	

## Technical viability: *Impacts of impurities & mitigation strategies*

Exchange membranes

- Developing tough polymer
- Engineering methods (e.g. refreshing the electrolyte)
- Hybridization with binder ionomers

Hydrocarbon polymer



Perfluorosulfonic acid ionomers

Electrode catalysts



Developing active & robust catalysts

Post-treatment (e.g., acidic washing)

Introducing protective shells

Full wrapping



# Technical viability

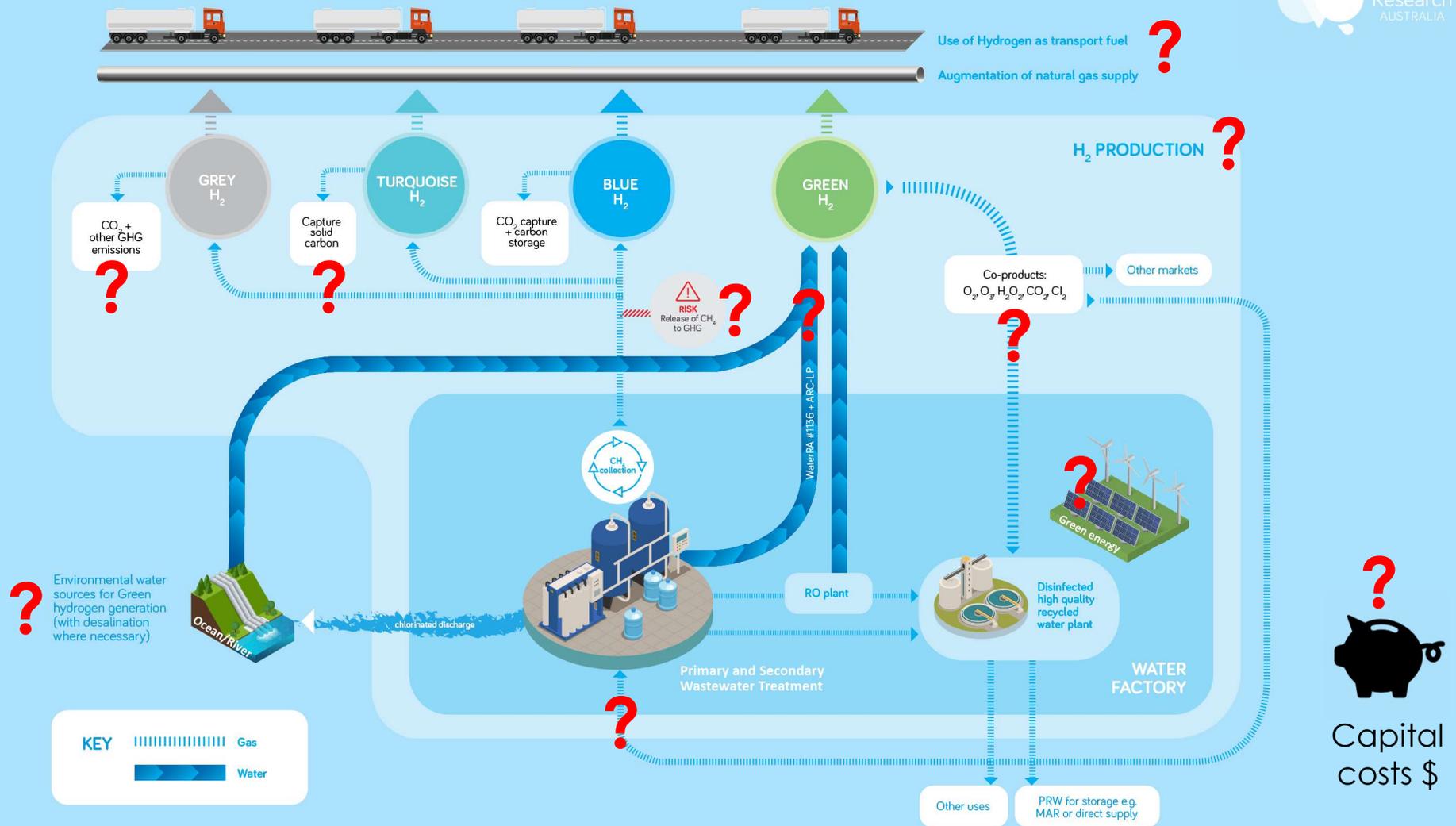
- Volumes of water required: Theoretically 9kg of H<sub>2</sub>O to produce 1 kg H<sub>2</sub>. At scale: estimated to be up to 90 kg electrolyser cooling
- Energy consumed for hydrogen production

Manufacturer	Technology Name	Operating Pressure	Hydrogen Flowrate	Energy Consumption	Operating Range	Water Consumption	Power	Electrical Efficiency
Manufacturer 1	HOGEN S10	13.8 bar <sub>g</sub>	0.265 Nm <sup>3</sup> /hr - 0.57kg/d	74 kWh/kg H <sub>2</sub>	0-100%	9.9 L/kg H <sub>2</sub>	1.1 kW	-
	HOGEN S20		0.53 Nm <sup>3</sup> /hr - 1.14 kg/d				2.2 kW	-
	HOGEN S40		1.05 Nm <sup>3</sup> /hr - 2.27 kg/d				4.3 kW	-
	H2	15 bar <sub>g</sub> / 30 bar <sub>g</sub> option	2 Nm <sup>3</sup> /hr	81 kWh/kg H <sub>2</sub>	0-100%	10.2 L/kg H <sub>2</sub>	8.1 kW	-
	H4		4 Nm <sup>3</sup> /hr	78 kWh/kg H <sub>2</sub>			16.1 kW	-
	H6		6 Nm <sup>3</sup> /hr	76 kWh/kg H <sub>2</sub>			23.7 kW	-
Manufacturer 2	ME 100/350	15 - 30 bar <sub>g</sub>	15-46.3 Nm <sup>3</sup> /hr	55 kWh/kg H <sub>2</sub>	32-100%	14.4 L/kg H <sub>2</sub>	225 kW	73%
	ME 450/1400	15 - 30 bar <sub>g</sub>	42-210 Nm <sup>3</sup> /hr	53 kWh/kg H <sub>2</sub>	20-100%	13.8 L/kg H <sub>2</sub>	1 MW	74%
	HCS 2MW	15 - 30 bar <sub>g</sub>	420 Nm <sup>3</sup> /hr	<53 kWh/kg H <sub>2</sub>	20-100%	16 L/kg H <sub>2</sub>	2 MW	>74%
	HCS 4MW	15 - 30 bar <sub>g</sub>	840 Nm <sup>3</sup> /hr			17 L/kg H <sub>2</sub>	4MW	
	HCS 10MW	15 - 30 bar <sub>g</sub>	2100 Nm <sup>3</sup> /hr			18 L/kg H <sub>2</sub>	10MW	
	S30/10	0 - 20 bar <sub>g</sub>	0.22 Nm <sup>3</sup> /hr	-	-	29 kg/hr	1 kW	78%
	S30/30	0 - 20 bar <sub>g</sub>	0.66 Nm <sup>3</sup> /hr	-	-	87 kg/hr	3 kW	
S30/50	0 - 20 bar <sub>g</sub>	1.10 Nm <sup>3</sup> /hr	-	-	145 kg/hr	5 kW		
Manufacturer 3	HyLYZER 200	30 bar <sub>g</sub>	200 Nm <sup>3</sup> /hr	<55 kWh/kg H <sub>2</sub>	5 - 100%	9 L/kg H <sub>2</sub>	-	-
	HyLYZER 250		250 Nm <sup>3</sup> /hr					
	HyLYZER 400		400 Nm <sup>3</sup> /hr	<54 kWh/kg H <sub>2</sub>				
	HyLYZER 500		500 Nm <sup>3</sup> /hr					
	HyLYZER 1000		1000 Nm <sup>3</sup> /hr	<51 kWh/kg H <sub>2</sub>				
Manufacturer 4	SILYZER 200	35 bar	225 Nm <sup>3</sup> /h	-	-	17 L/kg H <sub>2</sub>	1.25 MW	60-65%
	SILYZER 300	-	1300 kg/hr	-	0-100%	10 L/kg H <sub>2</sub>	~70 MW	>75.5 %

# Scalability of production processes

- The scalability of production processes is also a key concern:
  - Regional utilities: many plants distributed across a large geographic area.
- The risks associated with utility involvement in a hydrogen circular economy are also poorly defined:
  - Core business of a water utility?
- From a sustainability perspective a key potential risk is the allocation of water for hydrogen production in regions where water resource availability is subject to extreme variability due to climate change.
  - In this context, how can we not only secure water for electrolysis but continue to meet accessibility and affordability for other uses?

# Conceptual model of how the water industry can drive a circular economy



## Scalability:

WaterRA water industry consortium



SCALING GREEN  
HYDROGENCRC

Water “core partnership” workshop May 6<sup>th</sup> 2022 (online) - Themes:

- Water sources and their social licence;
- Technology needs for water reuse and beneficial co-products;
- Co-location opportunities (including renewable energy generation) and Integrated planning.

Contact me to join the workshop:  
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# Conclusion

- For successful integration of hydrogen and oxidant production into existing and newly developed water/wastewater treatment facilities, research questions regarding viability, scalability, sustainability and risks must be addressed.
- The potential gains are however promising, and adaptation of novel technologies for water reuse could facilitate a significant improvement in the sustainability and resilience of water treatment processes.



Innovation

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## CASE STUDY #3



**PROJECT:**  
Assessing hydrogen production viability and scalability  
—  
**REGION:**  
Australia-wide

### FUELLING THE FUTURE

Hydrogen production can add significant value to water operations, but the risks are poorly defined.

*Dr Arash Zamyadi, Karen Rouse and Liam Vaughan*

Integration of sustainable hydrogen production with the capture of associated greenhouse gases and carbon has the potential to facilitate an emerging circular economy. This could help the water industry achieve net zero carbon emissions and supply chain security for water treatment chemicals. Co-products such as oxygen, ozone and hydrogen peroxide are essential within a circular economy as sustainable fuels, chemical synthesis feedstocks, or as oxidising agents for advanced treatment processes.

Wastewater treatment plants (WWTPs) produce large quantities of recycled water and biogas, providing co-location opportunities for hydrogen production and alternative reuse prospects. This mitigates water source concerns for sustainable hydrogen, while reinforcing circular economy principles of wastewater as a valuable resource. The co-location of hydrogen production at existing WWTPs may reduce capital expenses by using existing infrastructure, land, and supply chains. Additionally, established recycled-water-based

**KEY CONSIDERATIONS**  
To understand the economic viability of hydrogen production, projected future demands for hydrogen and associated supply chain impacts must be defined. Capital costs present a significant barrier to entry, so a viability assessment must also consider the inherent value to prospective hydrogen producers of the secure water source, WWTP access to transport infrastructure, and land availability – including for renewable energy generation. The technical viability of recycled-water-based hydrogen production also presents many research questions, such as the volumes of recycled water required, optimal operating conditions, and the impacts of contaminants contained in wastewater. While WWTP processes effectively remove most contaminants, some persist, such as organic compounds, metal ions, nutrients, and inorganic debris, which could affect the performance of electrochemical reactions integral to hydrogen production. Performance of electrolysers improves when contaminants cause extreme pH values. But the low pH conditions ideal for hydrogen reduction are inconsistent with the high pH conditions optimal for water oxidation. This mismatch introduces process challenges which are further complicated by the degradation of electrocatalysts induced by extreme pH conditions. Further efforts are therefore necessary to investigate corrosion resistant catalysts and the operation of electrochemical water splitting under neutral conditions.

**SCALABILITY AND RISK**  
The scalability of production processes is a key concern, particularly for regional utilities that have many smaller WWTPs distributed across a large geographic area. The risks of utility involvement in a hydrogen circular economy are also not defined. From a sustainability perspective, a key risk is the allocation of water for hydrogen production in regions where water resource availability is variable due to climate change. Despite these knowledge gaps, the gains of integrating hydrogen and oxidant production look promising, with adaptation of novel technologies for water reuse having the potential to facilitate a significant improvement in the sustainability and resilience of water treatment processes. ■

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The co-location of hydrogen production at existing wastewater treatment plants may reduce capital expenses by using existing infrastructure, land, and supply chains.”  
Water Research Australia

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# Thank you

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