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Hydrogen production from non-potable water resources: A techno-economic investment and operation planning approach

J.C.T. Schoonderwoerd *,1, A. Belmondo Bianchi *,1, T. Zonjee, W.-S. Chen, S. Shariat Torbaghan

Environmental Technology, Wageningen University and Research, Building 118, Bornse Weilanden 9, Wageningen, 6708 WG, Gelderland, The Netherlands

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ABSTRACT

The production of hydrogen through water electrolysis facilitates large-scale energy storage, provides ancillary services, and supports the decarbonization of industries with hard-to-reduce emissions. As renewable energy adoption expands, the demand for these applications is increasing. However, water electrolysis currently faces challenges in cost competitiveness compared to other hydrogen production methods. Additionally, its reliance on potable water sources places additional strain on freshwater reserves. This study addresses these issues by exploring the economically optimal investment and operational strategy for hydrogen production using non-potable water sources. The goal is to maximize net profit through mathematical optimization, utilizing three advanced electrolysis technologies: alkaline electrolysis, proton exchange membrane electrolysis, and solid oxide electrolysis. The study examines three non-potable water sources: seawater, urban wastewater effluent, and rainwater. The model takes into account electricity market values from day-ahead and balancing markets, as well as the market values for hydrogen, oxygen, freshwater, and mixed solid salt. Two scenarios are analysed, reflecting varying levels of uncertainty in electricity price forecasts. Each scenario includes nine case studies, representing various combinations of water sources and electrolysis technologies. The results indicate that alkaline electrolysis and proton exchange membrane electrolysis are financially viable technologies, with potential annual net profits of up to 6.4 and 6.2 million euros, respectively. In contrast, solid oxide electrolysis incurs a negative net profit across all scenarios and is not economically viable under the given conditions. The main revenue sources are hydrogen sales and combined up-balancing and down-balancing services in electricity markets. Participation in the balancing market constitutes a significant portion (35 to 61%) of the total revenue in all cases with positive net profits, making it critical for economic viability. Rainwater is identified as the most cost-effective water source for hydrogen production. However, the costs associated with water treatment and brine management are minimal, contributing only 0.7 to 3.7% to the total cost of hydrogen production. Thus, differences in net profit are primarily attributed to the type of electrolysis technology used.

1. Introduction

1.1. Background and motivation

The integration of renewable energy sources into the power system introduces new challenges in managing the network (Shariat Torbaghan et al., 2018). Renewable energy sources are intermittent, fluctuating, uncertain, and location-specific (Azari et al., 2019). Thus, a high penetration level of renewable electricity necessitates increased flexibility in the power system. This flexibility is crucial to maintain a supply and demand balance and prevent renewable energy curtailment (Guerra et al., 2022). Energy storage can provide this flexibility (IRENA, 2018). However, storing electricity is expensive and difficult, especially at large volumes, as large-scale battery storage is costly and pumped-hydro storage is geographically constrained (Gür, 2018). A solution is to store electricity in a different format, such as hydrogen, a carbon-free energy carrier (Bosch et al., 2023). Hydrogen is a low-emission feedstock and fuel when produced by water electrolysis from renewable electricity (IEA, 2022). It has proven to be an excellent replacement for natural gas and other fossil fuels, particularly in heavy industry and long-distance, heavy-duty transport applications (Capurso et al., 2022).

The primary sources used to produce hydrogen are natural gas (48%), followed by oil (30%), and coal (18%) (Capurso et al., 2022). A sustainable alternative is hydrogen produced through water electrolysis (IRENA, 2021). This is an electrochemical process wherein high-purity water undergoes electrolysis, splitting into hydrogen and

* Corresponding authors.
E-mail addresses: julia.schoonderwoerd@gmail.com (J.C.T. Schoonderwoerd), alessio.belmondobianchidilavagna@wur.nl (A. Belmondo Bianchi).
[1] Contributed equally to this work.

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Nomenclature

Abbreviations

AEL	alkaline electrolysis
$aFRR$	automatic frequency restoration reserve
$ASTM$	American Society for Testing and Materials
BM	balancing market
DA	day-ahead market
FCR	frequency control reserve
FW	freshwater
IEX	ion exchange
LHV	lower heating value
$mFRR$	manual frequency restoration reserve
MSS	mixed solid salt
$PEMEL$	proton exchange membrane electrolysis
RO	reverse osmosis
RW	rainwater
$SOEL$	solid oxide electrolysis
SW	seawater
TDS	total dissolved solids
$UWWE$	urban wastewater effluent
ZLD	zero liquid discharge

Number sets

$\mathcal{T}$	time

Parameters

$\eta^{BR,wt-br\rightarrow FW}$	freshwater production rate brine recovery (m^3/m^3 brine)
$\eta^{RT,grid-el\rightarrow H_2}$	system energy consumption electrolysis (MWh/kgH_2)
$\eta^{W,ws-wt\rightarrow PW,wt-el}$	water recovery rate water treatment (–)
$\gamma^{H_2\rightarrow O_2}$	oxygen production rate electrolysis (kg/kgH_2)
$\gamma^{H_2\rightarrow PW,wt-el}$	pure water consumption rate electrolysis (m^3/kgH_2)
$\underline{f}^{el}$	lower bound electrolyzer operating range factor (fraction of nominal load) (–)
c^{fixed}	annual fixed cost of water treatment and electrolysis (€)
$c^{TDS,BR}$	TDS concentration of water treatment brine (g/m^3)
$c^{TDS,FW}$	TDS concentration of freshwater (permeate of brine recovery) (g/m^3)
$c^{TDS,PW}$	TDS concentration of pure water required by the electrolyzer (g/m^3)
$c^{TDS,W}$	TDS concentration of non-potable water source (g/m^3)
$capex^{el}$	investment costs electrolysis (€/MW)
$capex^{wt}$	investment costs water treatment (€)
$f^{fixedOM,el}$	fraction annual fixed operation and maintenance of total investment costs electrolysis (–)
k^{el}	electrolyzer capacity (MW)
lt	plant lifetime (year)
p^{bd}	brine disposal cost (€/m^3 brine)
p^{br}	brine recovery costs (€/m^3 freshwater)
p^{FW}	freshwater price (€/m^3)
p^{H_2}	hydrogen price (€/kg)
p^{MSS}	mixed solid salt price (€/kg)
p^{O_2}	oxygen price (€/kg)
p^{wt}	water treatment cost (€/m^3)
p^{W}	non-potable water price (€/m^3)
p_t^{DA}	day-ahead electricity price (€/MWh)
p_t^{DOWN}	down-balancing price (€/MWh)
p_t^{UP}	up-balancing price (€/MWh)
rr^{el}	ramp rate electrolyzer per 15 min (fraction of nominal load) (–)
sd^{el}	start-up delay factor electrolyzer (–)

Variables

Ω	net profit of the combined water treatment and hydrogen production plant (€)
$\overline{F}_t^{el}$	upper bound electrolyzer operating range factor (fraction of nominal load) (–)
$\overline{Q}_t^{RT,grid-el}$	maximum electricity consumption (MWh)
$\underline{Q}_t^{RT,grid-el}$	minimum electricity consumption (MWh)
C_t	total costs combined water treatment and hydrogen production plant, excluding fixed costs electrolysis (€)
$Q_t^{BR,wt-bd}$	quantity of brine to brine disposal system (m^3)
$Q_t^{BR,wt-br}$	quantity of brine to brine recovery system (m^3)
$Q_t^{DA,grid-el}$	quantity of electricity bought in the day-ahead market (MWh)
Q_t^{DOWN}	quantity of electricity for down-balancing (MWh)
Q_t^{FW}	quantity of freshwater produced (m^3)
$Q_t^{H_2}$	quantity of hydrogen produced (kg)
Q_t^{MSS}	quantity of mixed solid salt produced (kg)
$Q_t^{O_2}$	quantity of oxygen produced (kg)
$Q_t^{PW,wt-el}$	quantity of pure water produced (m^3)
$Q_t^{RT,grid-el}$	quantity of real-time electricity consumed (MWh)
Q_t^{UP}	quantity of electricity for up-balancing (MWh)
$Q_t^{W,ws-wt}$	quantity of non-potable water consumed (m^3)
R_t	total revenue combined water treatment and hydrogen production plant (€)
U_t	binary variable electrolyzer on or off (–)
W_t^{DOWN}	binary variable for down-balancing(–)
W_t^{UP}	binary variable for up-balancing(–)
Z_t	auxiliary binary variable to calculate maximum electrolyzer load (–)

oxygen when an electric current is applied (Qureshi et al., 2023). Obtaining pure water is essential because impurities can impede electrolysis and shorten the equipment's lifetime (David et al., 2019). Water electrolysis can utilize renewable electricity from the grid and thus does not have to involve carbon emissions in hydrogen production (Capurso et al., 2022).

Despite its advantages, water electrolysis for large-scale hydrogen production can stress the power system (Vargas-Ferrer et al., 2023), and it is not yet cost-competitive compared to grey hydrogen production methods (Capurso et al., 2022). However, water electrolysis can be seen as a significant source of flexibility, particularly through demand response (Nguyen et al., 2019). Demand response involves adjusting power consumption patterns to help balance fluctuations in supply and demand, incentivized by financial rewards (Babatunde et al., 2020). The additional capacity to offer ancillary services could potentially provide sufficient revenue to make water electrolysis a viable alternative to conventional production methods (Allidières et al., 2019). Another challenge is the intensification of global water scarcity since current water electrolysis technology uses drinking water to produce hydrogen. If the total hydrogen demand were met solely through water electrolysis, 617 million m^3 of water would need to be extracted annually, which equates to 1.3% of the energy sector's water demand (IEA, 2019).

The hydrogen demand is expected to increase in the coming years due to the rising demand for hydrogen in various sectors, such as the chemical and fuel industries and power supply and storage. Consequently, more water will need to be extracted to meet this growing demand (Capurso et al., 2022), which is predicted to reach 21 billion m^3/year for a mature hydrogen economy (Beswick et al., 2021). This represents a significant share of 43% of the current energy sector's water demand. The associated water stress and its effects, such as food insecurity, malnutrition, disease spread, and poverty, can be mitigated by using non-potable water sources. Non-potable water sources are alternative water sources not suitable for human consumption. Treatment is typically required to convert non-potable water into useable water, specifically for hydrogen production. Producing hydrogen from non-potable sources can directly reduce the demand for potable water. Furthermore, exploring alternative non-potable water resources and integrating treatment with the electrolysis process enables the placement of electrolyzers in remote areas with limited infrastructure, such as offshore locations, or in regions with low potable water availability. This facilitates distributed hydrogen production, enhancing accessibility and sustainability (Arthur et al., 2023).

Nguyen et al. (2019), Jang et al. (2022), and Juárez-Casildo et al. (2022) have investigated the economic performance of water electrolysis. Additionally, Lampert et al. (2022), Parra and Patel (2016), and Farag et al. (2020) have assessed the impact of providing ancillary services on the net profit of a hydrogen production plant. However, the ramp rate and start-up delay factors of water electrolysis technologies were not discussed. There is a dependency between the available electrolyzer operation range and the up and down status in the previous time instance, which is accounted for by modelling start-up times. Baumhof et al. (2023) considered cold start-up delays, although warm start-up constraints were ignored. Liu (2022) also incorporated flexibility-related factors, yet warm start-up delays and (non-potable) water treatment were excluded. Other studies in the literature have investigated the water treatment necessary to meet the electrolyzer standards. Oesterholt et al. (2017) accounted for both the water source and treatment in determining water demand. Simoes et al. (2021) investigated potential water sources for electrolysis considering treatment needs, reliability, availability, water losses, energy requirements, and costs, focusing on alkaline electrolysis (AEL) and proton exchange membrane electrolysis (PEMEL) technologies. The outcome is a qualitative decision-making framework concerning the choice of water source for hydrogen production. Winter et al. (2022) conducted a techno-economic and lifecycle analysis evaluating distributed near-point-of-use hydrogen production from non-traditional water sources. However, no mathematical optimization problem was used, and not all state-of-the-art electrolysis technologies and revenue streams were discussed in the two studies above.

From the literature above, it can be concluded that research related to the business case of a hydrogen production plant utilizing non-potable water sources and offering ancillary services has the following issues:

1. Studies on the economic performance of water electrolysis consider different system sizes and operation strategies, but the participation in various market segments and the impact of flexibility-related technical factors have not been thoroughly investigated.
2. Modelling approaches that optimize the scheduling of water electrolysis do not model warm start-up times, thus neglecting the dependency between the available electrolyzer operation range and the up and down status in the previous time instance.
3. Research covering a combined water treatment and hydrogen production plant did not consider revenue streams and did not include all state-of-the-art electrolysis technologies, impeding the evaluation of the economically optimal combination of electrolyzer and non-potable water source.

1.2. Contributions

To address the research gaps, this paper aims to investigate the economically optimal investment decision of hydrogen production from non-potable water resources, considering various water sources, water treatment, brine management, and different electrolysis technologies, as well as participation in the hydrogen, oxygen, freshwater (FW), mixed solid salt (MSS), and electricity markets. The optimal investment decision comprises two components: the optimal design and the optimal operation strategy. Design refers to a specific combination of non-potable water source and electrolysis technology, while operation strategy refers to how the combined water treatment and hydrogen production system interacts with the different markets. The contributions of the paper are as follows:

1. To solve an investment planning problem of a hydrogen production plant, incorporating diverse non-potable water resources, treatment technologies, and multiple markets for electricity, hydrogen, and by-products.
2. To solve operational aspects of this combined water treatment and hydrogen production plant on a quarterly resolution, resulting in the economically optimal operation strategy.
3. To introduce a novel approach to model the earlier mentioned dependency between available operation range and electrolyzer system status, using a set of binary decision variables and a novel mapping logic.
4. To perform sensitivity analysis on the importance of different factors to the business case.

1.3. Paper outline

The remainder of this paper is organized as follows: Section 2 provides the materials and methods used in this research. Section 2.1 describes the technologies, processes, resources, and markets involved in the model. Section 2.2 presents the modelling assumptions adopted in this study. Section 2.3 presents the mathematical formulation of the optimization model. This is followed by the results and discussion in Section 3. Section 4 concludes the paper and discusses directions for future research.

2. Material and methods

2.1. Combined water treatment and hydrogen production plant

2.1.1. Process description

The proposed model explores the economically optimal design and operation strategy of hydrogen production from seawater (SW), urban wastewater effluent (UWWE), and rainwater (RW). It examines various non-potable water sources, water treatment methods, brine management techniques, different electrolysis technologies, and participation in multiple markets. Fig. 1 provides an overview of the processes, input flows, output flows, and services involved. The operational strategy involves introducing non-potable water into a treatment process, resulting in pure water and concentrated brine. The brine can either be discharged or undergo further treatment, while the pure water is utilized in the electrolyzer to produce hydrogen gas and oxygen, both

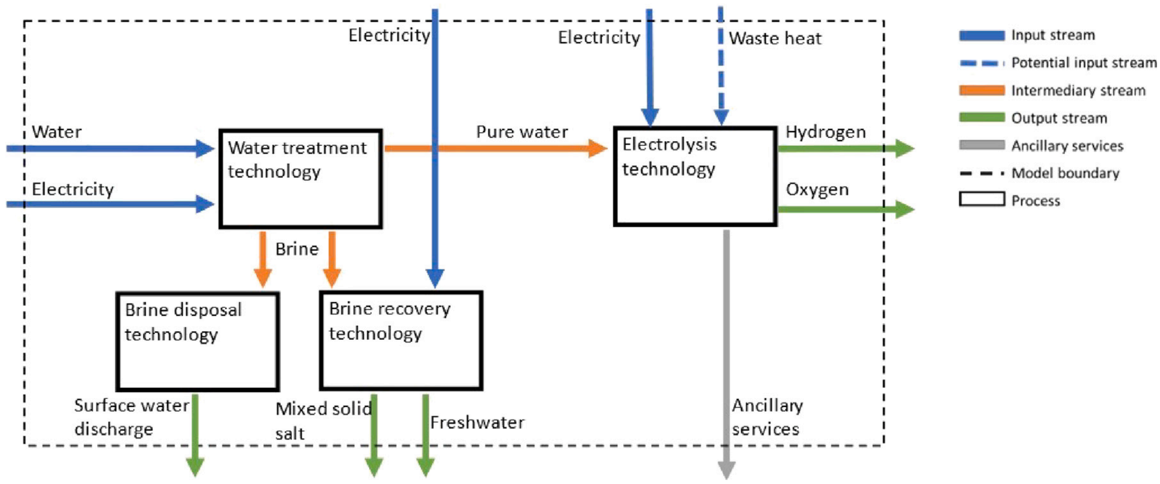

Fig. 1. Processes and flows involved in hydrogen production from non-potable water sources. 'Pure water' refers to the water treatment permeate that meets the electrolyzer water quality requirements.

of which can be sold as market products. Moreover, the electrolyzer offers ancillary services in the electricity market. Specific operational parameters vary depending on the electrolyzer technology, the chosen non-potable water source, and the market services under consideration, as elaborated in the following sections.

2.1.2. Electrolysis technologies

The electrolysis technologies differ in technical and economic aspects. AEL is the most mature and widespread technology (Capurso et al., 2022) with a cost advantage (Schiebahn et al., 2015). PEMEL is the most flexible technology, capable of quickly adjusting its power consumption and hydrogen production rate (Grigoriev et al., 2020). Solid oxide electrolysis (SOEL), still operating at lab-scale capacity, is the most efficient technology (Capurso et al., 2022). Table 1 gives an overview of the key characteristics. These characteristics serve as input for developing the operational limits and economic constraints in the optimization problem presented in Section 2.3. In this study, a simplified modelling approach has been chosen to model the three different electrolyzer technologies. For a more detailed description of the physics and technical modelling of the electrolyzers, readers are referred to Hu et al. (2022) for AEL, Subotić and Hochenauer (2022) for SOEL, and Ma et al. (2021) for PEMEL.

2.1.3. Water quality requirements

The electrolyzer technologies require deionized water of at least Type II (<1 μS/cm), as defined by the American Society for Testing and Materials (ASTM) (Mässgård and Jonsson, 2021). Specifically, the conductivity should be lower than 5 μS/cm, 0.2 μS/cm, and 1 μS/cm for AEL, PEMEL, and SOEL, respectively (Danish Energy Agency, Energinet, 2017). Often, total dissolved solids (TDS) concentration is used in literature instead of conductivity, representing the mineral or salt content of the water in g/m^3 or ppm (Voutchkov, 2012). The ratio between TDS concentration (g/m^3) and conductivity (μS/cm) is typically 0.5, although it varies depending on the temperature and sodium chloride content (Voutchkov, 2012).

2.1.4. Water treatment technologies

Water treatment technologies convert non-potable water with high TDS levels to deionized water demanded by water electrolysis. Reverse osmosis (RO) is the most common membrane treatment technology. The authors of Di Martino et al. (2021) and Feria-Díaz et al. (2021) show that the benefits of RO are the compact design, low costs, and relatively low energy consumption. Note that the salinity of SW, UWWE, and RW falls within the feed limits of RO (Panagopoulos, 2021c). An additional polishing step, such as ion exchange (IEX), is often added after RO to obtain ASTM Type II water (Lee et al., 2016). In this research, combined RO and IEX treatment steps were considered for SW and UWWE, while RW was treated solely by IEX, as further discussed in Section 2.2.3. The treatment process eventually yields Type II water and a concentrated brine stream.

2.1.5. Brine management

Brine has high salinity and may contain residues, heavy metals, and chemicals from water treatment, causing harmful effects when released into the environment (Ihsanullah et al., 2021). Therefore, the model also considers the management of the water treatment brine. Regarding brine management, surface water discharge and zero liquid discharge (ZLD) were selected. Surface water discharge is a common practice and the cheapest brine disposal method (Panagopoulos et al., 2019). The electricity consumption of surface water discharge is negligible. On the other hand, ZLD is a brine recovery method where a combination of desalination technologies, in this case, brine concentrators and brine crystallizers, yields high-quality FW and MSS (Panagopoulos et al., 2019). ZLD is a more sustainable option than surface water discharge since it maximizes water recovery and minimizes waste generation.

2.1.6. Market participation

A combined water treatment and hydrogen production plant can participate in the hydrogen, oxygen, electricity, FW, and MSS markets. Hydrogen is mainly applied in the chemical and petrochemical sectors (IEA, 2022). The global hydrogen market is expected to increase from \$160 billion in 2022 (Markets and Markets, 2022) to almost \$12 trillion by 2050 (Oni et al., 2022). Oxygen can be used for industrial applications such as the production of steel, pulp and paper, and metal refining (Hurskainen, 2017). It can also be used for medical applications if the oxygen gas has a purity higher than 99.5% (Hurskainen, 2017). Brine recovery yields two potentially marketable products: FW and MSS. The produced FW has a TDS concentration lower than 10 g/m^3, which can be used for drinking water applications (Panagopoulos et al., 2019). There are multiple uses for MSS. It can be disposed of eco-friendly (Panagopoulos et al., 2019), further processed to extract valuable materials such as metals (lithium, rubidium, etc.) (Panagopoulos, 2022) and salts (NaCl, $CaCl_2$, etc.), or reused as a de-icing agent for roads (Panagopoulos, 2021a).

Table 1
Key characteristics of AEL, PEMEL and SOEL.

	AEL	PEMEL	SOEL
Electrolyte	20–40 wt% KOH[a]	Water[a]	Steam[a]
Conductive ions	OH^{-} [b]	H^{+} [b]	O^{2-} [b]
Cell temperature	60–90 °C[c]	50–80 °C[c,d,e]	700-900 °C[c]
Typical pressure	10–30 bar[c]	20–50 bar[a,c]	1–15 bar[a,c]
Current density	0.25–0.45 A/cm^2 [c]	1.0–2.0 A/cm^2 [c]	0.3–2.0 A/cm^2 [a]
System efficiency (LHV)	Conventional: 66%[e] Improved: 80%[f]	62%[e]	Electric heaters: 61% External waste heat: 88%[e,g]
Specific energy consumption (LHV)	Conventional: 51 kWh/kg H_2 Improved: 42 kWh/kg H_2	54 kWh/kg H_2	Electric heaters: 55 kWh/kg H_2 External waste heat: 38 kWh/kg H_2
Operating range (% of nominal load)	15%–100%[h]	5%–100%[b]	0%–100%[c]
Ramp rate	Ramp up: 7–17%/s Ramp down: 10–25%/s[i]	40%/s[i]	<30%/h[b]
Cold start-up time	20–60 min[a]	5 min[i]	>60 min[a]
Warm start-up time	1–5 min[c]	<10 s[i]	15 min[c]
System response	Seconds[a]	Milliseconds[a]	Seconds[a]
Investment costs[l]	800–1500 €/kW[a,c]	1400-2100 €/kW[a,c]	2000–2500 €/kW[j]
Annual operating costs[m] (% of investment costs)	2%–4%[c,e,k]	3%–5%[c,e]	3%[e]

[a] Tenhumberg and Büker (2020).
[b] Liu (2022).
[c] Buttler and Spliethoff (2018).
[d] IEA (2019).
[e] Jang et al. (2022).
[f] Hodges et al. (2022).
[g] Mässgård and Jonsson (2021).
[h] ASA (2021).
[i] Nguyen et al. (2019).
[j] Wang et al. (2019).
[k] van Leeuwen and Mulder (2018).
[l] The investment costs data is based on Buttler & Spliethoff (2018) and Wang et al. (2019). Buttler & Spliethoff (2018) give the installed system costs, including feedwater management, while the investment cost data of Wang et al. (2019) was not specified.
[m] Electricity, deionized water, labour, and KOH (AEL) costs are not considered in the annual operating costs. The annual operating costs consist of service and maintenance costs (2%) and other operating costs (1%).

2.1.7. Electricity market structure

The Dutch power market can be divided into four market segments: the forward market, day-ahead market (DA), intraday market, and balancing market (BM). This study focuses on the DA due to its significant trading volume and numerous bidding parties. Additionally, it investigates the BM since deviations resulting from renewable energy penetration occur in real-time (van Leeuwen and Mulder, 2018). In the DA, the market regulator receives 24 hourly bids from market players one day before delivery. Once the market is cleared, hourly prices correspond to the highest bid accepted by the market regulator. As real-time approaches, the estimation of power demand and supply becomes more accurate, potentially resulting in deviations from the DA schedule. These deviations are managed by the transmission grid operator within the BM. The three main BM products include frequency control reserve (FCR), automatic frequency restoration reserve (aFRR), and manual frequency restoration reserve (mFRR). FCR is automatically activated, and the total bid capacity is available within 30 s (ENTSO-E, 2018).

In the Netherlands, the required FCR amount is determined by European regulation and is auctioned weekly (pay-as-bid) (Alshehri et al., 2019). For aFRR, the full capacity activation takes a maximum of five minutes (Alshehri et al., 2019). It is auctioned every 15 min through a combination of contracted bids and non-contracted voluntary bids (Alshehri et al., 2019). mFRR reaches the total bid capacity within 15 min. This frequency control type is used for large or more prolonged frequency deviations. It is activated manually and operates on capacity contracts rather than bid-obligation contracts (TenneT, 2024). This study focuses on the short-term approach where electrolyzers can voluntarily bid every 15 min, offering either up (decreasing electricity consumption and hydrogen production) or down balancing (increasing electricity consumption and hydrogen production). Therefore, the electrolyzer participates in aFRR.

2.2. Modelling assumptions

This section outlines the modelling assumptions used to formulate the economically optimal design and operational strategy of hydrogen production as a mathematical optimization problem. The problem is formulated as a mixed-integer linear optimization problem involving four sets of integer variables. It is solved across nine case studies: (1) SW-AEL, (2) UWWE-AEL, (3) RW-AEL, (4) SW-PEMEL, (5) UWWE-PEMEL, (6) RW-PEMEL, (7) SW-SOEL, (8) UWWE-SOEL, and (9) RW-SOEL. Each case study represents a distinct combination of water source and electrolysis technology, as detailed in Section 2.1.

2.2.1. Technical and economic parameters

Technical conversion and efficiency parameters characterize the underlying processes. These data, along with flexibility-related electrolyzer characteristics, the costs of input streams (electricity and water), process expenditures (water treatment and electrolysis), and the prices of output streams (hydrogen, oxygen, ancillary services, brine, FW, MSS), constitute the model parameters (see Table 2 and Table 3), detailed further in subsequent sections.

Table 2
Technical parameters for combined water treatment and hydrogen production optimization.

Parameter	Explanation	Value	References
$\eta^{RT,grid-el\rightarrow H_2}$	System energy consumption electrolysis	AEL: 0.042 MWh/kgH_2 PEMEL: 0.054 MWh/kgH_2 SOEL: 0.038 MWh/kgH_2	Hodges et al. (2022), Jang et al. (2022)
$\gamma^{H_2\rightarrow PW,wt-el}$	Pure water consumption rate electrolysis	0.010 m^3/kg H_2	Bhandari and Shah (2021), Systems (2021), Jang et al. (2022), ASA (2021)
$\gamma^{H_2\rightarrow O_2}$	Oxygen production rate electrolysis	8 kg/kg H_2	IEA (2019), Jang et al. (2022)
k^{el}	Electrolyzer capacity	10 MW	–
rr^{el}	Ramp rate electrolyzer per 15 min (fraction of nominal load)	AEL: 1 PEMEL: 1 SOEL: 0.075	Liu (2022), Nguyen et al. (2019)
$\underline{f}^{el}$	Lower bound electrolyzer operating range factor (fraction of nominal load)	AEL: 0.15 PEMEL: 0.05 SOEL: 0	Buttler and Spliethoff (2018), Liu (2022), ASA (2021)
sd^{el}	Start-up delay factor electrolyzer	AEL: 0.33 PEMEL: 0 SOEL: 0	Buttler and Spliethoff (2018), Nguyen et al. (2019)
$\eta^{W,ws-wt\rightarrow PW,wt-el}$	Water recovery rate water treatment	SW: 0.50 UWWE: 0.50 RW: 0.99	Winter et al. (2022)
$\eta^{BR,wt-br\rightarrow FW}$	Freshwater production rate brine recovery	0.9895 m^3/m^3 brine	Panagopoulos (2021a)
$c^{TDS,W}$	TDS concentration non-potable water source	SW: 35,000 g/m^3 UWWE: 1,500 g/m^3 RW: 400 g/m^3	Greenlee et al. (2009), Hofman-Caris et al. (2019), Oni et al. (2022)
$cTDS, PW$[a]	Maximum TDS concentration of pure water required by the electrolyzer	AEL: 2.5 g/m^3 PEMEL: 0.1 g/m^3 SOEL: 0.5 g/m^3	Danish Energy Agency, Energinet (2017)
$cTDS, FW$	TDS concentration of freshwater (permeate of brine recovery)	10 g/m^3	Panagopoulos et al. (2019), Tong and Elimelech (2016)

[a] The TDS concentration of the pure water required by the electrolyzer is calculated by multiplying the conductivity by 0.5, which is the typical ratio of TDS to conductivity for (desalination) permeate water (Voutchkov, 2012).

Table 3
Economic parameters for combined water treatment and hydrogen production optimization.

Parameter	Explanation	Value	References
p^{H_2}	Hydrogen price	2 €/kg	European Commission (2020), IEA (2019), Rasul et al. (2022), Younas et al. (2022)
p^{O_2}	Oxygen price	0.080 €/kg	Breyer et al. (2015)
p^{FW}	Freshwater price	0.87 €/m^3	Waternet (2022)
p^{MSS}	Mixed solid salt price	0.00 €/kg	–
p^{W}	Non-potable water price	0.00 €/m^3	–
p_t^{DA}	Day-ahead electricity price	Historical data — 2021 [€/MWh]	ENTSO-E (2022a)
p_t^{UP}	Up-balancing price	Historical data — 2021 [€/MWh]	ENTSO-E (2022b)
p_t^{DOWN}	Down-balancing price	Historical data — 2021 [€/MWh]	ENTSO-E (2022b)
$capex^{wt}$	Investment costs water treatment	SW: 575,000 € UWWE: 500,000 € RW: -	Simoes et al. (2021)
$capex^{el}$	Investment costs electrolysis	AEL: 1,150,000 €/MW PEMEL: 1,750,000 €/MW SOEL: 2,250,000 €/MW	Buttler and Spliethoff (2018)
$f^{fixedOM,el}$	Fraction annual fixed operation and maintenance of capex electrolysis	0.03 /year	Jang et al. (2022)
lt	Plant lifetime	20 years	–
p^{wt}	Water treatment cost[a]	SW: 2.84 €/m^3 UWWE: 2.64 €/m^3 RW: 2.64 €/m^3	Winter et al. (2022)
p^{bd}	Brine disposal cost[b]	0.175 €/m^3 brine	Panagopoulos et al. (2019)
p^{br}	Brine recovery cost[b]	1.13 €/m^3 freshwater produced	Panagopoulos (2021a), Panagopoulos et al. (2019)

[a] Electricity costs are already included.
[b] Capital and operating costs, thus also including the electricity costs.

2.2.2. Non-potable water sources

Non-potable water is assumed to be readily available at the presumed location. Operations beyond treatment, such as pumping and storage in the water network, are not included in the model due to their dependency on the specific water source location. Costs related to water storage and pumping are also excluded. Additionally, non-potable water is assumed to be provided free of charge. The water quality parameters assumed in the model are 35,000 g TDS/m^3 for SW (Jones et al., 2019), 1500 g TDS/m^3 for UWWE (Oni et al., 2022), and 400 g TDS/m^3 for RW (Hofman-Caris et al., 2019).

2.2.3. Water treatment

All non-potable water sources require treatment before entering the electrolyzer. SW and UWWE are treated using a combined RO and IEX process. RW, falling within the feed range of IEX (1–800 g TDS/m^3), is exclusively treated with this technology (Voutchkov, 2012). The water recovery rate is 99% for IEX and 50% for RO (Winter et al., 2022). Winter et al. (2022) analysed the purification costs of various non-traditional water sources to achieve ASTM Type II water quality. The costs include operational expenses of RO combined with ion exchange resin polishing, excluding pre-treatment and maintenance costs. The cost of the polishing step for water already treated by RO is 2.64 €/m^3 (Winter et al., 2022). Based on the findings of Winter et al. (2022), assumed treatment costs are 2.84 €/m^3 for SW, 2.64 €/m^3 for UWWE, and 2.64 €/m^3 for RW. Furthermore, the investment costs for RO are 575,000 € for SW and 500,000 € for brackish water (Simoes et al., 2021). These investment costs are amortized without considering interest rates.

2.2.4. Brine management

Regarding brine management, the model assumes surface water discharge via diffusers, incurring a capital and operating cost of 0.175 €/m^3 of brine (Panagopoulos et al., 2019). Alternatively, ZLD is achieved through brine concentrators and crystallizers, with a capital and operating cost of 1.13 €/m^3 of produced FW (Panagopoulos, 2021a). It is important to note that electricity consumption for water treatment and brine management is integrated into the cost factor and not separately accounted for. Additionally, electricity consumption constitutes less than 0.3% of the total system electricity consumption (Winter et al., 2022). The ZLD process achieves a water recovery rate of 99%, producing FW with a TDS concentration of 10 g/m^3, priced at 0.87 €/m^3. According to Panagopoulos (2021b), MSS from SW desalination can be sold for 0.005 $/kg. Since the quality and application of MSS are uncertain in this study, the MSS price is assumed to be 0. Furthermore, based on findings from Panagopoulos (2021c) and Panagopoulos and Haralambous (2020), the TDS quantity in the MSS stream reflects the MSS volume, as TDS measures the salt concentration in SW. While further investigation is needed to confirm if this assumption applies to UWWE and RW, it does not impact the model as no value is assigned to MSS.

2.2.5. Electrolysis process

An electrolyzer with a capacity of 10 MW is assumed to operate as a price taker in a perfectly competitive electricity market using electricity price data from the Netherlands in 2021. Additional assumptions include the following: no electricity consumption when hydrogen production is idle; hydrogen can be dispatched directly to the network; only warm start-ups are considered; and the plant has a lifetime of 20 years. Moreover, (warm) start-up delays, ramp rates, and operating load ranges are considered, as these technical factors related to flexibility determine the ability to provide ancillary services. The warm start-up time for SOEL is disregarded due to its operational range of 0 to 100%, enabling standby mode operation with minimal energy consumption.

The electrolysis process is characterized by efficiency and conversion factors. For every 1 kg of hydrogen produced, 0.01 m^3 of pure water is consumed, yielding 8 kg of oxygen. The efficiency of an alkaline capillary-fed electrolyzer, exemplified by a newly developed technology as reported by Hodges et al. (2022), is assumed to represent AEL efficiency, despite its current small-scale status. Regarding SOEL, it is assumed that a waste heat source is available at no cost, reflecting an optimistic scenario with a system energy efficiency of 88% (lower heating value, LHV). However, if electric resistance heaters are used to produce high-temperature steam instead of utilizing waste heat, the system efficiency would decrease to 61% (LHV).

Finally, the following cost and price assumptions are applied: the market price of hydrogen is 2.00 €/kg, and the market price of oxygen is 0.080 €/kg. Electrolysis investment costs are set at 1,150,000 €/MW (AEL), 1,750,000 €/MW (PEMEL), and 2,250,000 €/MW (SOEL). Annual fixed operation and maintenance costs of the electrolyzer are calculated as 3% of the respective investment costs. The hydrogen price aligns with that of hydrogen produced through steam methane reforming with carbon capture and storage, a commercially viable technology.

2.3. Mathematical problem formulation

The problem is mathematically formulated as a mixed-integer linear optimization program with Eqs. (1) to (26). The objective is to maximize the total net profit of the integrated water treatment and hydrogen production plant while adhering to technical and economic constraints.

$$\max_{\zeta} \Omega = -C^{fixed} + \sum_{t\in T}[R_t - C_t] \tag{1}$$

$s.t.$

$$C^{fixed} = \frac{capex^{wt}}{lt} + k^{el} capex^{el} f^{fixedOM,el} + k^{el}\frac{capex^{el}}{lt} \tag{2}$$

$$R_t = Q_t^{H_2} p^{H_2} + Q_t^{O_2} p^{O_2} + Q_t^{UP} p_t^{UP} + Q_t^{DOWN} p_t^{DOWN} + Q_t^{FW} p^{FW} + Q_t^{MSS} p^{MSS} \quad \forall t \in \mathcal{T} \tag{3}$$

$$C_t = Q_t^{DA,grid-el} p_t^{DA} + Q_t^{W,ws-wt} p^{W} + Q_t^{PW,wt-el} p^{wt} + Q_t^{BR,wt-bd} p^{bd} + Q_t^{FW} p^{br} \quad \forall t \in \mathcal{T} \tag{4}$$

$$Q_t^{RT,grid-el} = Q_t^{DA,grid-el} + Q_t^{DOWN} - Q_t^{UP} \quad \forall t \in \mathcal{T} \tag{5}$$

$$W_t^{UP} + W_t^{DOWN} \le 1 \quad \forall t \in \mathcal{T} \tag{6}$$

$$Q_t^{UP} \le W_t^{UP}\frac{k^{el}}{4} \quad \forall t \in \mathcal{T} \tag{7}$$

$$Q_t^{DOWN} \le W_t^{DOWN}\frac{k^{el}}{4} \quad \forall t \in \mathcal{T} \tag{8}$$

$$Q_t^{H_2} = \frac{Q_t^{RT,grid-el}}{\eta^{RT,grid-el\rightarrow H_2}} \quad \forall t \in \mathcal{T} \tag{9}$$

$$Q_t^{PW,wt-el} = Q_t^{H_2}\gamma^{H_2\rightarrow PW,wt-el} \quad \forall t \in \mathcal{T} \tag{10}$$

$$Q_t^{O_2} = Q_t^{H_2}\gamma^{H_2\rightarrow O_2} \quad \forall t \in \mathcal{T} \tag{11}$$

$$-\frac{k^{el}}{4} rr^{el} \le Q_t^{RT,grid-el} - Q_{t-1}^{RT,grid-el} \le \frac{k^{el}}{4} rr^{el} \quad \forall t \in \mathcal{T} \tag{12}$$

$$-\frac{k^{el}}{4} rr^{el} \le Q_t^{DA,grid-el} - Q_{t-1}^{RT,grid-el} \le \frac{k^{el}}{4}\cdot rr^{el} \quad \forall t \in \mathcal{T} \tag{13}$$

$$\underline{Q}_t^{RT,grid-el} \le Q_t^{RT,grid-el} \le \overline{Q}_t^{RT,grid-el} \quad \forall t \in \mathcal{T} \tag{14}$$

$$\underline{Q}_t^{RT,grid-el} = \frac{k^{el}}{4}\underline{f}^{el} U_t \quad \forall t \in \mathcal{T} \tag{15}$$

$$\overline{F}_t^{el} = (1 - sd^{el})U_t + sd^{el} U_{t-1} - sd^{el} Z_t \quad \forall t \in \mathcal{T} \tag{16}$$

$$Z_t \le U_{t-1} \quad \forall t \in \mathcal{T} \tag{17}$$

$$Z_t \le 1 - U_t \quad \forall t \in \mathcal{T} \tag{18}$$

$$Z_t \ge U_{t-1} - U_t \quad \forall t \in \mathcal{T} \tag{19}$$

$$\overline{Q}_t^{RT,grid-el} = \frac{k^{el}}{4}\overline{F}_t^{el} \quad \forall t \in \mathcal{T} \tag{20}$$

$$\underline{Q}_t^{RT,grid-el} \le Q_t^{DA,grid-el} \le \overline{Q}_t^{RT,grid-el} \quad \forall t \in \mathcal{T} \tag{21}$$

$$Q_t^{W,ws-wt} = \frac{Q_t^{PW,wt-el}}{\eta^{W,ws-wt\rightarrow PW,wt-el}} \quad \forall t \in \mathcal{T} \tag{22}$$

$$Q_t^{BR,wt-bd} = Q_t^{W,ws-wt} - Q_t^{PW,wt-el} - Q_t^{BR,wt-br} \quad \forall t \in \mathcal{T} \tag{23}$$

$$Q_t^{FW} = Q_t^{BR,wt-br} \eta^{BR,wt-br \to FW} \qquad \forall t \in \mathcal{T} \quad (24)$$

$$Q_t^{MSS} = \frac{c^{TDS,BR} Q_t^{BR,wt-br} - c^{TDS,FW} Q_t^{FW}}{1000} \qquad \forall t \in \mathcal{T} \quad (25)$$

$$c^{TDS,BR} = \frac{c^{TDS,W} - c^{TDS,PW} \eta^{W,ws-wt \to PW,wt-el}}{1 - \eta^{W,ws-wt \to PW,wt-el}} \quad (26)$$

Note that $\zeta := \{Q_t^{RT,grid-el}, \underline{Q}_t^{RT,grid-el}, \overline{Q}_t^{RT,grid-el}, Q_t^{DA,grid-el}, Q_t^{UP}, Q_t^{DOWN}, Q_t^{H_2}, Q_t^{PW,wt-el}, Q_t^{O_2}, Q_t^{W,ws-wt}, Q_t^{BR,wt-bd}, Q_t^{BR,wt-br}, Q_t^{FW}, Q_t^{MSS}, \overline{F}_t^{el}, U_t, Z_t, W_t^{UP}, W_t^{DOWN} | \forall t \in T\}$ is the set of all optimization decision variables. T refers to the set of time instances t, defined based on 15-minute intervals (i.e., the same time basis at which the aFRR market in BM is cleared).

The objective function (1) is to maximize the net profit of the plant (Ω) as the sum of the total revenue (R_t) minus the total variable costs (C_t) and the fixed costs of the electrolyzer and water treatment (C^{fixed}). Constraint (2) defines the total fixed costs as the sum of the annual investment costs of water treatment, annual fixed operation and maintenance costs of electrolysis, and the annual investment costs of electrolysis. Constraints (3) and (4), respectively, define R_t and C_t as the product of quantity (Q) and the associated price (p) of the resource in question.

Constraint (5) defines the amount of electricity consumed by the electrolyzer in real-time (i.e., $Q_t^{RT,grid-el}$) as the net sum of electricity procured in DA ($Q_t^{DA,grid-el}$), plus down-balancing (Q_t^{DOWN}) and minus up-balancing (Q_t^{UP}). The binary variables W_t^{UP} and W_t^{DOWN} in constraint (6) prohibit offering both up- and down-balancing services at the same time. W_t^{UP} (W_t^{DOWN}) takes 1 if up-balancing (down-balancing) is offered and 0 otherwise. Therefore, at every time instance, $t \in T$, an electrolyzer can participate in either up- or down-balancing or just stand by. The amount of up- and down-balancing the electrolyzer unit can offer to the market at every time instance is bounded to the maximum power rating of the unit that is enforced by (7) and (8).

Constraint (9) describes the quantity of hydrogen produced ($Q_t^{H_2}$) as a function of real-time electricity consumption by the electrolyzer. Likewise, Eqs. (10) and (11) define the quantity of pure water consumption ($Q_t^{PW,wt-el}$) and oxygen production ($Q_t^{O_2}$) as a function of produced hydrogen.

Constraint (12) enforces the electrolyzer ramp rate. It limits the extent to which the electricity consumption of the electrolyzer can vary in two consecutive time steps. The ramp rate is calculated by multiplying the maximum load with the ramp rate factor (rr^{el}), which is a technical characteristic of the electrolyzer given by the manufacturer of the technology in use. In this work, rr^{el} is defined as a fraction of the nominal load.

Constraint (13) represents a supervision limit. It limits the amount of flexibility the electrolyzer can offer to the market by its feasible ramp rate. An upper cap to the DA bid size is imposed as this cannot exceed the amount of real-time electricity consumed during the previous time instance plus or minus the maximum ramp-up or ramp-down, respectively.

Constraint (14) imposes the operation range of the electrolyzer unit where the lower bound is defined in (15) and the upper bound in (16)–(20). The factor denoting the upper operating bound ($\overline{F}_t^{el}$) considers warm start-up time after a shut-down. This is relevant for AEL since this technology needs 5 min to start up (other technologies can be re-engaged instantly). Therefore, if an AEL is shut down at a time instance, it will not be able to produce hydrogen during the first 5 min (out of 15 min) of the next time instance, resulting in a start-up delay factor (sd^{el}) of 0.33. Where the binary variable $U_t = 1$ implies that the electrolyzer is on and off otherwise, the auxiliary binary variable Z_t is defined to account for the effect of start-delay on the maximum load after a shut-down. If an AEL electrolyzer is off at the previous time instance and is switched on in the next one, Z_t takes the value 0. This applies the start-up delay factor to the upper operating bound of the AEL technology. If the AEL is off during two consecutive time instances Z_t, and thus $\overline{F}_t^{el}$, take value 0. Consecutively, constraint (21) poses an upper and lower bound on the DA bid size of AEL electrolyzers.

Constraint (22) determines the quantity of non-potable water ($Q_t^{W,ws-wt}$) by dividing the quantity of pure water by the recovery rate of the treatment process. Next, Eq. (23) represents the water balance of the treatment process. The quantity of FW produced by brine recovery (Q_t^{FW}) is determined using the FW production rate according to Eq. (24). Finally, Eqs. (25) and (26) determine the quantity of MSS (Q_t^{MSS}). For this purpose, the TDS concentration in brine ($c^{TDS,BR}$) is calculated based on the TDS concentration of the non-potable water, the TDS concentration of the pure water fed to the electrolyzer, and the treatment water recovery rate. The quantity of MSS is then calculated as the TDS mass difference between the input brine and the produced FW (25).

3. Results and discussion

3.1. Scenarios

The investment and operational planning of the hydrogen production plant are simulated over one year (with a 15-minute resolution) for two scenarios and nine case studies. These scenarios are designed to account for uncertainties related to imperfect market forecasts. A schematic representation of the modelling procedure is illustrated in Fig. 2.

In scenario 1, problem (1–26) is solved considering perfect DA, up-balancing, and down-balancing price forecasts. The amount of up-balancing and down-balancing is bounded by the maximum electrolyzer capacity, according to constraints (7) and (8). Constraints (12), (13), (14), and (21) limit the amount of real-time and DA electricity by the ramp rate, start-up delay, and the operating range of the electrolyzer, which prevents too large bids that the system would technically not be able to deliver. This scenario serves as a preliminary milestone for evaluating a more realistic scenario. It highlights which combination of non-potable water sources and electrolysis technology should be avoided. The rationale behind this approach is that if an investment strategy lacks economic feasibility even with perfect price forecasts, investors will inevitably avoid such strategies in the real world, where profits would fall short of the projections made in this scenario.

Scenario 2 represents the most realistic case, where optimization is divided into two parts solved sequentially: day-ahead and real-time modelling steps. In the first step, referred to as scenario 2-DA, the focus is on optimizing the DA bidding strategy without considering the BM. This implies that the DA bidding strategy is no longer based on perfectly forecasted BM prices as opposed to scenario 1. To prevent real-time response from taking place during scenario 2-DA, decision variables Q_t^{UP} and Q_t^{DOWN} are set to 0 for every time instance. Additionally, a 3% error is introduced to the DA prices to account for market uncertainties. This error reflects a realistic DA forecast error and is modelled as uniformly distributed white noise (Zonjee and Torbaghan, 2023). In the second step, referred to as scenario 2-RT, the optimal DA schedule established in scenario 2-DA is treated as a fixed input. In this step the electrolyzer engages in the BM, offering up- and down-balancing services.

3.2. Numerical results

Fig. 3 shows the optimization results for the nine case studies and two scenarios. When the combined water treatment and hydrogen production plant is operated according to scenario 1, the net profit amounts to 6.4 M€ for AEL, 6.2 M€ for PEMEL, and −0.17 to −0.21 M€ for SOEL. Systems including AEL are most profitable, regardless of the non-potable water source. Still, SW is the most expensive in each of the experiments, followed by UWWE and, finally, RW. The primary revenue sources for AEL and PEMEL are hydrogen sales, with respective

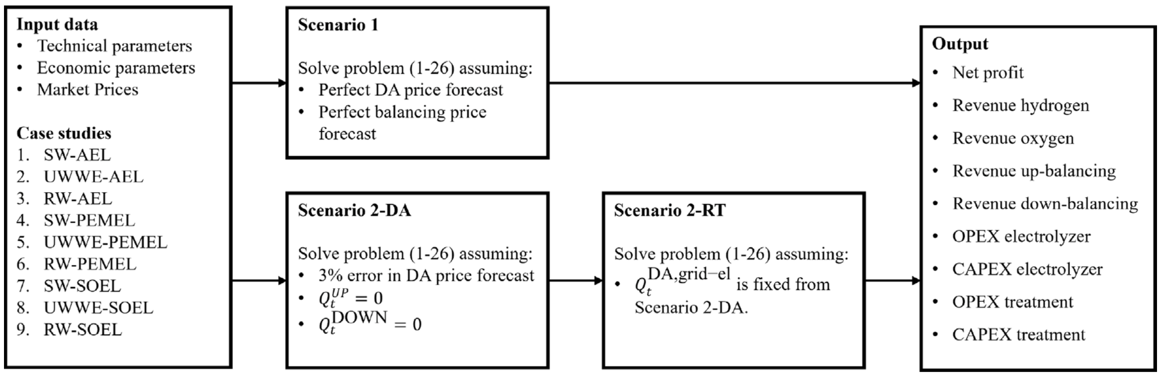

Fig. 2. Schematic overview of modelling process for the nine case studies and two optimization scenarios.

figures of 3.7 M€ and 2.8 M€, as well as from up-balancing (2.8 M€ and 3.3 M€) and down-balancing (2.0 M€ and 2.3 M€). Differently, for SOEL the revenue from up-balancing and down-balancing services amounts to 0.5 M€ and 0.2 M€, respectively, which is significantly lower than other technologies. Revenue from oxygen sales is 1.2 M€ for AEL, 0.9 M€ for PEMEL, and 0.7 M€ for SOEL. Regarding costs, AEL incurs 2.4 M€ for DA electricity purchases, while PEMEL and SOEL spend 1.7 M€ and 1.9 M€ respectively. Furthermore, a significant cost factor for all three technologies is the capital and operational expenses of the electrolyzer, which amounts to 0.9 M€, 1.4 M€, and 1.8 M€ for AEL, PEMEL, and SOEL, respectively. Additional information regarding the cost and revenue in scenario 1 is provided in Table A.1 in Appendix A.

Considering the most profitable case study, which is RW combined with AEL, hydrogen is the largest revenue stream with a share of 38%. Moreover, up- and down-balancing revenue comprises 50% of the total revenue. The differences in profit are mainly affected by the electrolysis technology type. SOEL has the highest investment and fixed operation and maintenance costs. Also, it is the least flexible technology due to the low ramp rate, resulting in a negative business case. PEMEL is the most flexible technology with a fast ramp rate, wide operating range and short start delay. AEL is adequately flexible relative to the needs of the BM and has a cost advantage. Water treatment and brine management account for only 0.7–2.5% of the total costs. This indicates the impact of the water source on the total costs of hydrogen production is low, making non-potable water sources worth considering if abundantly available. They are a sustainable and environmentally friendly solution to reduce pressure on freshwater reserves. The model always selects brine disposal instead of brine recovery. The situation can be reversed if a brine disposal penalty is considered or there is revenue from brine recovery (see Section 3.3). Despite the minor profit differences between the non-potable water sources, it should be noted that RW is the most cost-effective water source. It has the lowest salinity, so it can be treated only with IEX, resulting in the following benefits: the water treatment does not involve additional costs of RO, and the water recovery rate is high.

It is noted that in scenario 2-DA, all case studies yield a negative net profit. While the specific results for scenario 2-DA are not detailed here, upon implementing Scenario 2-RT, the aggregated net profit amounts to 5.5 M€ for AEL, 4.6 M€ for PEMEL, and −0.6 M€ for SOEL, as illustrated in Fig. 3. This suggests that offering up- and down-balancing services is critical to making the hydrogen production plant economically viable. Furthermore, the net profits in scenario 2-RT are comparatively lower than in scenario 1 for all case studies. Consistent with scenario 1, in scenario 2-RT the DA electricity purchase and the capital and operational cost of the electrolyzer are major cost factors, accounting for 27%–58% and 39%–70% of the total costs, respectively. The impact of the different non-potable water sources on the net profit is limited, with a contribution of 0.8-3.7% of the total costs. Case studies incorporating AEL demonstrate the most favourable economic performance, whereas those involving SOEL exhibit the least favourable performance.

Zooming in on the economically most feasible case studies (RW-AEL), in scenario 1, hydrogen sales constitute approximately 38% of the total revenue, whereas in scenario 2-RT, they account for 49%. The notable difference lies in the limited up-balancing revenue in scenario 2-RT compared to scenario 1. In scenario 1, revenue from up-balancing exceeds that from down-balancing, whereas in scenario 2-RT, it is much smaller. This disparity can be attributed to the uncertainty in price forecasts and the unknown up- and down-balancing prices when determining the amount of electricity to purchase in the DA under scenario 2-DA. This shows that uncertainty in price forecasts plays an important role in determining the market participation strategy. Also, it suggests that the benefits of providing up-balancing services can only be realized if there is an economic advantage in purchasing additional electricity in the DA. In scenario 2-DA, economic opportunities arise when revenues from hydrogen and oxygen sales exceed the costs of DA electricity. While this is sufficient to enable some participation in the BM, the lack of perfect knowledge about balancing prices effectively limits the up-balancing revenue in scenario 2-RT compared to scenario 1.

Fig. 4 highlights the large volumes traded in the BM, occurring in scenario 2-RT after the predetermined amount of DA electricity is bought. Consistent with earlier observations, the down-balancing magnitude surpasses that of up-balancing by a factor of 11 for AEL, 18 for PEMEL, and 7 for SOEL. This reaffirms the limitation on up-balancing purchases in scenario 2-RT. Additionally, there is a notable increase in real-time electricity consumption by water electrolysis compared to the quantity bid in the DA for both AEL and PEMEL. Specifically, the down-balancing volume reaches 55 GWh for AEL and 69 GWh for PEMEL, which is respectively two and four times higher compared to the volume bid in the DA. This indicates a preference for utilizing additional electricity procured in the BM rather than solely relying on DA electricity for real-time hydrogen and oxygen generation.

In contrast, SOEL demonstrates limited real-time electricity consumption, primarily due to its lower ramp rate, which limits its operational flexibility. With a ramp rate of 7.5% per 15 min, SOEL lags behind AEL and PEMEL. Consequently, SOEL's participation in the BM is the lowest among all case studies. In contrast, PEMEL, with its wider operating range and absence of a warm start-up delay, purchases the majority of electricity in the BM, surpassing AEL in this aspect. The results demonstrate the effectiveness of the proposed approach in

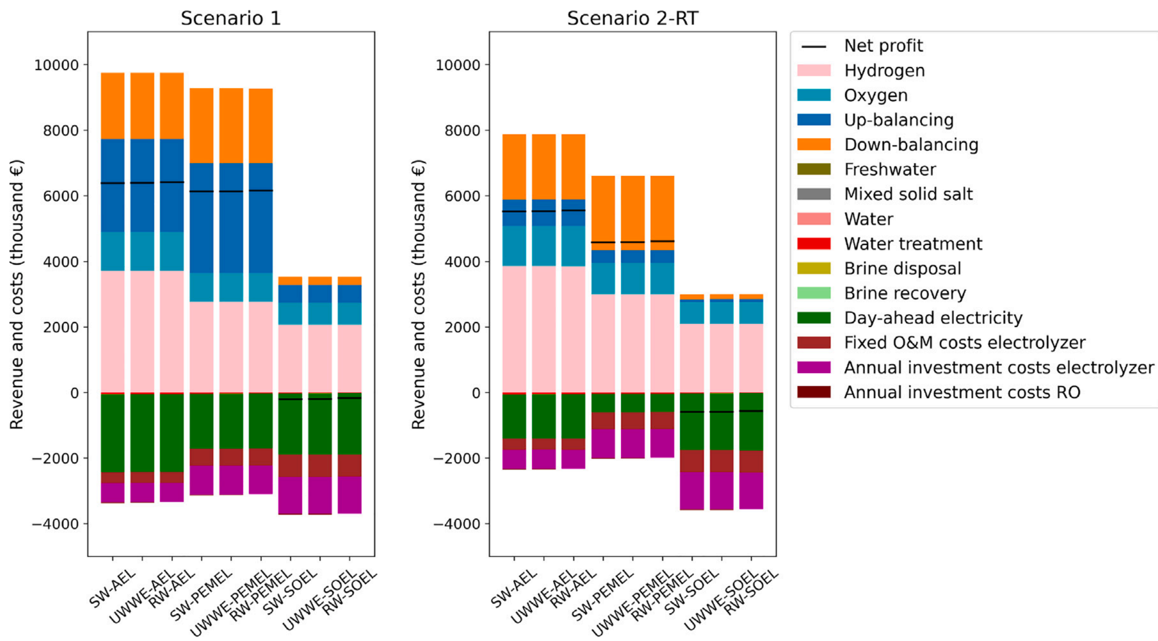

Fig. 3. Cost and revenue breakdown of hydrogen production from non-potable water resources for scenario 1 (left) and scenario 2-RT (right).

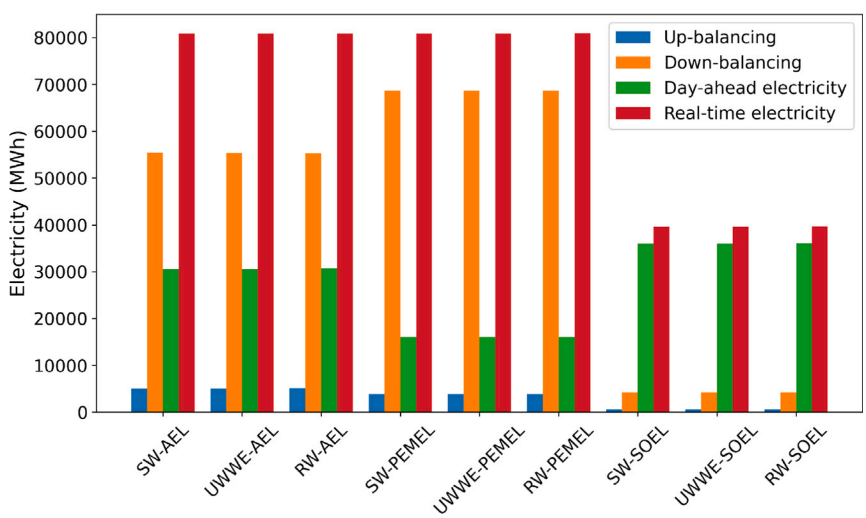

Fig. 4. Bidding strategy in the DA and BM of scenario 2-RT.

determining the optimal participation strategy in the BM. They also highlight the economic advantage of participating in the BM when the technology exhibits sufficient operational flexibility. Supplementary data corresponding to Fig. 4 is provided in Table A.2 in Appendix.

3.3. Sensitivity analysis

The sensitivity of the results was studied by performing a one-factor-at-a-time sensitivity analysis of the output of scenario 2-RT. According to Panagopoulos (2021b), who investigated the business case of ZLD, MSS produced through recovery of SW desalination brine can be sold for 0.005 €/kg. Allocating this market value to MSS suggests that brine recovery is preferred over brine disposal for hydrogen production from SW and RW. Panagopoulos (2021b) considered drinking water prices of 3.2 \$/m^3 and 3.84 \$/m^3, corresponding to the drinking water prices in Greece and Cyprus, respectively. Raising the FW price from 0.87 €/m^3 to 2 €/m^3 also resulted in a preference for brine recovery. When no additional profit is gained, the combined water treatment and hydrogen production plant will opt for surface water discharge, which has adverse environmental effects. Moreover, it was demonstrated that if RW is treated by the same water treatment technologies as SW and UWWE, namely RO and IEX, the water treatment and brine management costs increase by factors of 1.5 and 99, respectively. The difference in water treatment cost is attributed to the investment costs of RO, while the high brine management costs are due to the reduced water recovery rate. Nevertheless, the impact on the total net profit is less than 1%. Finally, selecting a more pessimistic estimation for the efficiency of AEL (66%) and SOEL (61%) decreased the net profit by approximately 7.5% and 12%, respectively. Despite this, hydrogen production systems that include AEL remained the most profitable, while those including SOEL resulted in a negative business case.

3.4. Reflection

Results indicate that AEL exhibits the most favourable economic performance. This is largely attributed to its lower capital cost (1.15 M€) compared to PEMEL (1.75 M€) and SOEL (2.25 M€). Another crucial factor contributing to AEL's economic efficiency is its comparable ramp rate to PEMEL (i.e., 1) and higher than SOEL (0.075), along with a relatively fast warm start-up time (i.e., 1–5 min). The results of scenario 2-RT demonstrate in the one-year duration of the study, there are 31 (UWWE-SOEL) to 85 (UWWE-PEMEL) instances where no hydrogen is produced for more than one hour, while there are 9 (SW-SOEL, UWWE-SOEL, RW-SOEL) to 22 (SW-AEL, SW-PEMEL, UWWE-PEMEL) instances where no hydrogen is produced for more than two hours. During those instances, the cold start-up time becomes relevant. The cold start-up time is at least 20 min for AEL and 60 min for SOEL, while PEMEL has a cold start-up time of only 5 min which offers a competitive advantage. However, the optimization model only considered warm start-ups. It was also assumed that standby mode does not require electricity. As outlined in Section 1.1, the cold-start-up time is addressed in Baumhof et al. (2023). Furthermore, an addition to the model could be considering heat integration and FW reuse. FW could be treated until it reaches the water quality required by the electrolyzers and since brine recovery is a thermal process, residual heat produced in water electrolysis can be used. According to Danish Energy Agency, Energinet (2017), 16.4%, 26.4%, and 0% of the input energy is converted to recoverable heat in AEL, PEMEL, and SOEL, respectively. Nevertheless, if this heat is recovered, determining the reduction in energy demand of brine recovery is complex due to the dynamic operation of the water electrolysis technologies.

Moreover, the study focused on three non-potable water sources that are considered widely available. Results demonstrated that the most economical water source across all scenarios is RW, followed by UWWE, and SW. The difference in treatment costs originates from the different capital investments required for the treatment process. RW undergoes treatment solely by IEX, while UWWE and SW require investment in an RO facility bringing an additional cost of 500 k€ and 575 k€ respectively. Another significant factor affecting treatment cost is the TDS concentration, which is significantly higher in SW ($3.5 \cdot 10^4$ g/m^3) and UWWE ($1.5 \cdot 10^3$ g/m^3) compared to RW ($4.0 \cdot 10^2$ g/m^3). This, in turn, leads to higher operational costs for treatment and brine management. However, it should be noted that RW is only accessible in certain regions. It is weather-dependent, so this water flow is less predictable than UWWE. Also, it was not investigated if it is legally allowed to use RW, as well as UWWE, for large-scale hydrogen production, which possibly competes with other applications. Besides, water network costs were excluded, while these location-specific costs can be significant. For example, Simoes et al. (2021) reported lower costs for UWWE compared to RW due to the high RW collection costs. Finally, an important condition to reduce the pressure on potable water reserves is to produce and consume the hydrogen locally, which is also advantageous considering hydrogen transportation costs. When hydrogen is combusted or employed in a fuel cell, clean water is generated. Via this pathway, the water quality of the non-potable water is upgraded, and the water cycle is closed. However, when hydrogen is imported or exported, the water cycle becomes out of balance, causing a net shortage or surplus in certain regions, further aggravating water scarcity.

It should be noted that the findings of this study rely on the assumptions that were made. First of all, the investment costs were approximated based on available data. Economies of scale effects were neglected. That is, as system size increases and/or electrolyzer technology becomes more mature, the investment cost will become lower than what is assumed in this paper. The electrolysis investment costs thus represent the maximum investment costs. On the opposite side, IEX, brine disposal, and brine recovery costs were not based on water quality characteristics but on the water quantity. Particularly considering surface water discharge, which is the brine disposal method, it can be more reasonable to price these based on the amount of salt discharge. This can especially be the case if adverse environmental effects are accounted for.

3.4.1. Computational considerations

All simulations are implemented in Python 3.9/Gurobi. The computer used ran Windows 10 64-bit with an Intel Core i5-1135G7 CPU clocking at 2.4 GHz, and 8 GB of RAM.

4. Conclusion and future work

This study proposes a novel modelling approach to investigate the economically optimal design and operation strategy for hydrogen production using non-potable water resources. The problem is formulated as a mixed-integer linear optimization program. The objective is to maximize the total net profit of the integrated water treatment and hydrogen production plant. The problem considers the physical and economic characteristics of different electrolysis technologies, water treatment processes, brine management systems, and participation in multiple markets for electricity, hydrogen, and by-products. Three electrolysis technologies, AEL, PEMEL, and SOEL, were evaluated using three widely available non-potable water sources: SW, UWWE, and RW. Two scenarios were analysed, reflecting varying levels of uncertainty in electricity price forecasts. Each scenario included nine case studies, representing different combinations of water sources and electrolysis technologies. Results obtained through numerical simulation allowed us to draw the following conclusions:

- The proposed model can be used to study the optimal investment and operational strategy for hydrogen production from non-potable water sources, aiding decision-making for system operators and investors.
- AEL and PEMEL resulted in profitable business cases, whereas SOEL showed a negative net profit. The main revenue streams were hydrogen sales and the combined provision of up-balancing and down-balancing services.
- AEL was identified as the most economically viable electrolysis technology resulting in a net profit of up to 6.4 M€. The comparative advantage of AEL is its low capital cost, high efficiency, and operational flexibility.
- Revenue from BM participation was crucial for economic viability, contributing 35%–61% of total revenue in profitable scenarios.
- The most economically efficient water source was RW. Water treatment and brine management contributed only 0.7–3.7% of the total system costs across all scenarios. Brine disposal was preferred over brine recovery unless economic incentives were provided.

One promising extension of this work involves incorporating accurate forecast error models for BM prices to assess the true business potential of each combination of water source and electrolysis technology. Additionally, future research should consider important technical aspects such as non-potable water availability, pre-treatment, and the impacts

Table A.1
Cost and revenue of hydrogen production from non-potable water resources in k€ for scenario 1 and scenario 2-RT.

	SW-AEL	UWWE-AEL	RW-AEL	SW-PEMEL	UWWE-PEMEL	RW-PEMEL	SW-SOEL	UWWE-SOEL	RW-SOEL
Scenario 1									
Net profit	6375	6383	6411	6130	6137	6163	−206	−200	−174
Hydrogen	3710	3710	3710	2764	2764	2764	2069	2071	2072
Oxygen	1187	1187	1187	885	885	885	662	663	663
Up-balancing	2833	2833	2832	3340	3340	3339	544	544	544
Down-balancing	2022	2022	2022	2284	2284	2284	249	249	249
Freshwater	0	0	0	0	0	0	0	0	0
Mixed solid salts	0	0	0	0	0	0	0	0	0
Water	0	0	0	0	0	0	0	0	0
Water treatment	−53	−49	−49	−39	−36	−36	−29	−27	−27
Brine disposal	−3	−3	0	−2	−2	0	−2	−2	0
Brine recovery	0	0	0	0	0	0	0	0	0
Day-ahead electricity	−2372	−2372	−2371	−1673	−1673	−1673	−1871	−1872	−1874
Fixed operation and maintenance costs electrolyzer	−345	−345	−345	−525	−525	−525	−675	−675	−675
Annual investment costs electrolyzer	−575	−575	−575	−875	−875	−875	−1125	−1125	−1125
Annual investment costs reverse osmosis	−29	−25	0	−29	−25	0	−29	−25	0
Scenario 2-RT									
Net profit	5519	5526	5550	4578	4585	4606	−597	−591	−564
Hydrogen	3852	3853	3851	2996	2996	2997	2083	2084	2087
Oxygen	1233	1233	1232	959	959	959	667	667	668
Up-balancing	797	799	802	385	387	380	95	95	95
Down-balancing	1995	1995	1994	2267	2267	2267	149	149	149
Freshwater	0	0	0	0	0	0	0	0	0
Mixed solid salts	0	0	0	0	0	0	0	0	0
Water	0	0	0	0	0	0	0	0	0
Water treatment	−55	−51	−51	−43	−40	−40	−30	−28	−28
Brine disposal	−3	−3	0	−3	−3	0	−2	−2	0
Brine recovery	0	0	0	0	0	0	0	0	0
Day-ahead electricity	−1351	−1354	−1359	−555	−557	−557	−1730	−1732	−1735
Fixed operation and maintenance costs electrolyzer	−345	−345	−345	−525	−525	−525	−675	−675	−675
Annual investment costs electrolyzer	−575	−575	−575	−875	−875	−875	−1125	−1125	−1125
Annual investment costs reverse osmosis	−29	−25	0	−29	−25	0	−29	−25	0

of water quality on membrane and catalyst activity. Further studies could also consider the investment and operational costs of water reclamation and storage systems. Moreover, exploring alternative water treatment and brine management technologies could unlock additional revenue streams by recovering valuable resources from brine, making recovery more profitable compared to surface water discharge. Lastly, understanding the efficiency and degradation effects of the dynamic operation of electrolysis technologies is crucial. This knowledge will facilitate the development of a more realistic and effective investment and operational strategy for hydrogen production from non-potable water sources.

CRediT authorship contribution statement

J.C.T. Schoonderwoerd: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **A. Belmondo Bianchi:** Writing – review & editing, Visualization, Supervision, Software, Methodology, Data curation, Conceptualization. **T. Zonjee:** Writing – review & editing, Visualization, Supervision, Software, Methodology, Conceptualization. **W.-S. Chen:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Conceptualization. **S. Shariat Torbaghan:** Writing – review & editing, Validation, Supervision, Software, Resources, Project administration, Methodology, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix. Supplementary data

See Tables A.1 and A.2.

Table A.2
Bidding strategy in the DA and BM in MWh for scenario 1 and scenario 2-RT.

	SW-AEL	UWWE-AEL	RW-AEL	SW-PEMEL	UWWE-PEMEL	RW-PEMEL	SW-SOEL	UWWE-SOEL	RW-SOEL
Scenario 1									
Up-balancing	8142	8142	8135	10 270	10 265	10 262	1981	1978	1978
Down-balancing	62 395	62 395	62 404	68 296	68 300	68 303	6172	6174	6174
Day-ahead electricity	23 656	23 656	23 650	16 605	16 600	16 597	35 121	35 148	35 164
Real-time electricity	77 909	77 909	77 918	74 631	74 635	74 638	39 312	39 344	39 359
Scenario 2-RT									
Up-balancing (MWh)	5051	5051	5089	3855	3875	3850	589	587	589
Down-balancing (MWh)	55 407	55 381	55 301	68 640	68 630	68 635	4213	4206	4208
Day-ahead electricity (MWh)	30 539	30 577	30 655	16 100	16 133	16 130	35 954	35 979	36 028
Real-time electricity (MWh)	80 895	80 907	80 866	80 885	80 888	80 915	39 578	39 598	39 648

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