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Circular Economy Approaches to Produced Formation Water: Opportunities and Challenges

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Abstract

As exploitation fields mature, oil and gas production generates huge quantities of formation water-brine, the handling of which is becoming an increasing problem in the petroleum industry. In line with the concepts of the circular economy, alternative uses for formation water (brine) are therefore being considered in order to reduce freshwater consumption. One of these is the production of "green" hydrogen in electrolysers. In electrolysis, high-purity water is crucial for the efficiency and longevity of the systems, which is why water treatment processes are required. The direct use of brine in electrolysis systems is associated with problems such as corrosion and contamination of equipment. In the paper, brine produced during oil and gas exploitation in the eastern part of the Drava Depression is analysed. The required power of the electrolysis system of 418 MW to convert all the produced water that is now returned to the fields is a challenge, but a model that utilises some of the water and uses the excess electricity to convert the produced water into hydrogen could be a viable option.

Keywords: formation water; Drava Depression; hydrocarbon exploitation; hydrogen; electrolysis; circular economy.

1. Introduction

The volatility of energy prices, the dependence of most countries on energy imports and increasing climate change have placed renewable energy at the centre of national energy strategies. In this context, the use of sustainable energy sources based on the circular economy is the right way forward for a clean energy transition.

According to the International Renewable Energy Agency (IRENA), a scenario in which the average global temperature increase is limited to 1.5 °C considers the climate-friendly production of 614 million tonnes of hydrogen (H_2) by 2050, which means that hydrogen would cover 12% of total energy demand (**IRENA, 2022; IRENA & Bluerisk 2023**). Hydrogen can be used as a raw material to produce steel, ammonia, methanol, fertilisers and synthetic fuels, but also to power vehicles or store seasonally limited renewable energy.

The production of "brown" or "grey" hydrogen, considering that hydrogen is produced from coal by gasification or from methane by methane steam reforming (SMR), causes significant greenhouse gas emissions, which is not in line with climate-neutral targets. "Blue" hydrogen refers to "brown" and "grey" hydrogen combined with carbon capture, utilisation and storage (CCUS), which limits greenhouse gas emissions. There are other hydrogen production technologies, but only SMR with biogas and nuclear electrolysis have reached a certain level of commercialisation (**IRENA & Bluerisk 2023**).

"Green" hydrogen is considered an acceptable alternative to fossil resources as it can be produced by water electrolysis, in in which water is split into O_2 and H_2 using renewable electricity. The main advantages of this technology are that no greenhouse gases (GHG) are released into the atmosphere, while the required electricity can be generated from renewable energy sources such as wind, solar, hydrothermal sources or biomass (**Kabir et al., 2023).**

According to **Marouani et al. (2023),** many challenges arise when it comes to production costs, ensuring adequate infrastructure for storage, distribution and use in various applications, and the development of innovative technologies. Specialised techniques are needed to prevent hydrogen leakage and improve safety measures in the storage, transport and use of hydrogen. In addition, many aspects of "green" hydrogen production are still questionable, such as land utilisation or actual greenhouse gas emissions considering carbon lifecycle analysis (**IRENA & Bluerisk 2023**). Currently, the production costs for 1 kg of H_2 from fossil fuels are \$1.2, while the costs for 1 kg of green H_2 are \$4 (**Blay-Roger et al., 2024**).

One of the most important prerequisites for water electrolysis is the need for high-purity water. According to the American Society for Testing and Materials (ASTM), the minimum requirement is Type II deionised water (DI water) (resistance >1 MΩ cm), while ASTM Type I DI water (>10 MΩ cm) is preferred for high purity (99.99%) hydrogen. According to one estimate, 21 billion m^3 of fresh, pure water will be needed by 2030 to achieve the desired hydrogen economy. Since clean water is needed to produce green hydrogen and clean water is fast becoming a scarce resource, the question arises as to whether it can be called "green". It is important to realise that accessible freshwater only accounts for <1% of the water on our planet. About 99% is almost exclusively salt water or water trapped in ice in the polar regions (**Abdel-Aal et al., 2010**). Such available salt water appears to be more convenient for use as an electrolysis feedstock for hydrogen production. As a 10 MW electrolyser requires 50-60 m^3/day of clean water, salt water treatment would be crucial for the production of sustainable green hydrogen (**Farràs et al., 2021;** ***https://www.alfalaval.com/***). Therefore, using salt water with the right desalination technology seems to be an optimal option to preserve scarce freshwater supplies. Another option is the direct utilisation of salt water as electrolyser feed.

The paper analysed the possibility of utilising the formation water (brine) produced in the exploitation of hydrocarbons in electrolysers to produce hydrogen. An overview of the available technologies was given, and an example of the water produced from seven (7) hydrocarbon fields in the Eastern Part of the Drava Depression was used as a case study.

2. Formation water (brine) production

Highly mineralized water, produced during hydrogen production, also known as "formation water" or "brine", is the main waste produced in oil and gas exploitation activities. This can be water that is naturally present in the reservoir and flood water that is injected into the oil field. The increase in oil and gas production has raised a global environmental issue related to the disposal of produced brine–water (**Nasiri & Jafari, 2017**). Produced water, which generally increases in volume as the field matures, can be 98% contained in the produced fluid (**Neff et al., 2011; Al-Ghouti et al., 2019**). The global average of this ratio is around 3 (barrels of water):1 (barrels of oil). As a result, the management of produced water is becoming an increasingly important part of oil and gas operations (**Wenzlick & Siefert, 2020**). Worldwide, daily brine production has reached 250 million barrels and is expected to reach 600 million barrels in the next ten years (**McCabe, 2020; Amakiri et al., 2022**).

After being produced within the formation fluid, the water is separated and treated (de-oiled) before being discharged. The limits for the discharge of produced water are often regulated and the oil content is specified in the oil content limits. According to the report by the International Association of Oil and Gas Producers (IOGP), which collected and published environmental data from its 40 operations, 46% of produced water is discharged, while 54% of produced water is reinjected underground. Even 79% of the water produced from onshore activities in 2021 was injected underground to maintain reservoir pressure or for disposal. Around 22% of the water discharged comes from offshore operations and 78% from onshore operations. The overall average oil content of produced water discharges in 2021 totalled 14.4 mg/l, with an average value of 17.1 mg/l for offshore activities and 5.7 mg/l for onshore activities (**Figure 1**; **IOGP, 2022**).

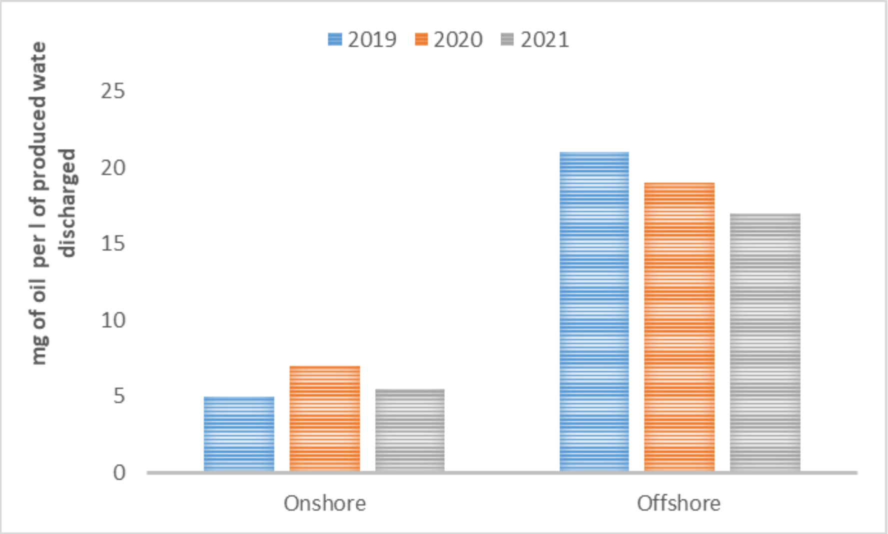


Figure 1: Oil content of produced water discharges (according to **IOGP, 2022**)

Although in general almost two-thirds of the de-oiled water extracted offshore is discharged into the sea, this is handled differently in different regions, i.e. companies operating in the Russia and Central Asia region reported reinjection of all water quantities produced offshore, while in Africa only one-fifth was reinjected (**Figure 2**).

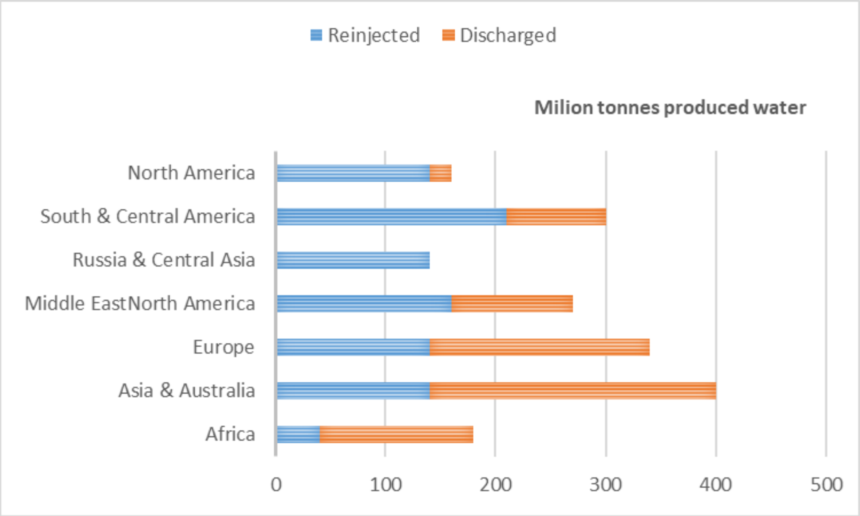
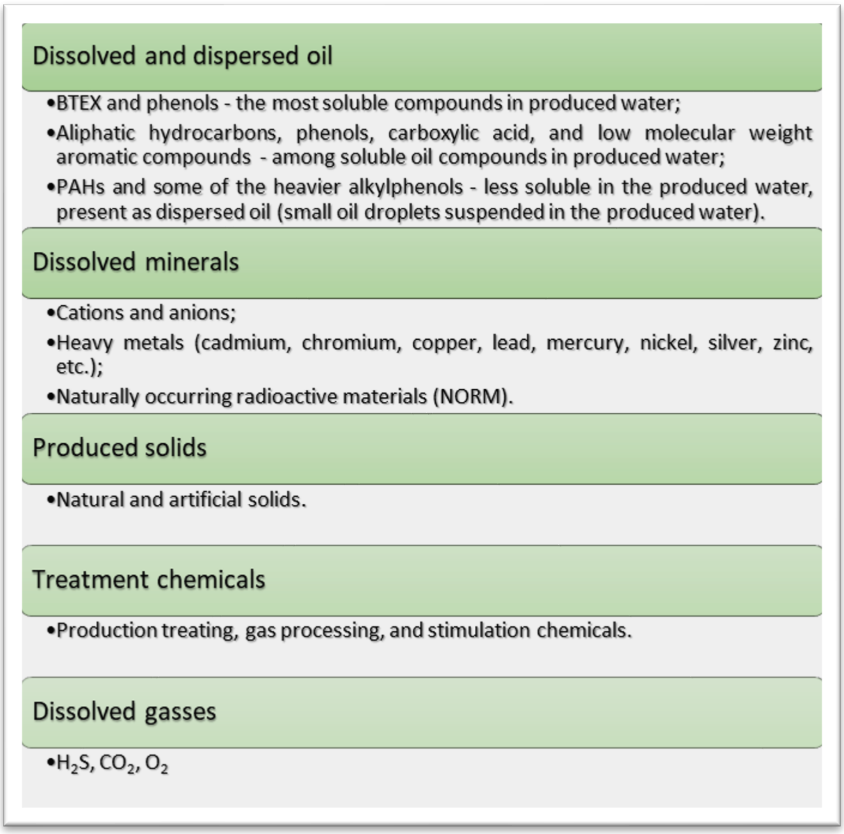


Figure 2: Quantities of formation water reinjected and discharged by region (according to **IOGP, 2022**)

The composition and properties of the produced water vary depending on reservoir (**Alley et al., 2011**). The properties of produced saline water change and its volume increases over the life of the field. The main constituents of produced water generally include dissolved and dispersed oil, dissolved minerals, solids, treatment chemicals and dissolved gases. **Tables 1 and 2** show the main components of oil field brine and its average content.

Table 1: Main constituents in oil field brine (**Fakhru'l-Razi et al., 2009; Amakiri et al, 2022**)



Dissolved and dispersed oil

- BTEX and phenols - the most soluble compounds in produced water;
- Aliphatic hydrocarbons, phenols, carboxylic acid, and low molecular weight aromatic compounds - among soluble oil compounds in produced water;
- PAHs and some of the heavier alkylphenols - less soluble in the produced water, present as dispersed oil (small oil droplets suspended in the produced water).

Dissolved minerals

- Cations and anions;
- Heavy metals (cadmium, chromium, copper, lead, mercury, nickel, silver, zinc, etc.);
- Naturally occurring radioactive materials (NORM).

Produced solids

- Natural and artificial solids.

Treatment chemicals

- Production treating, gas processing, and stimulation chemicals.

Dissolved gasses

- H_2S, CO_2, O_2

Table 2: Average oilfield brine content (**Ahmadun et al, 2009; Nasiri & Jafari, 2017**)

PARAMETER	**VALUE (mg/l)**
Total organic carbon, TOC	0-1500
Chemical Oxygen Demand, COD	1220
Total Suspended Solids, TSS	1.2-1000
Total oil (mg/l)	2-565
Benzene, Toluene, Ethylbenzene and Xylen, BTEX	0.39-35
Chloride	80-200000
Bicarbonate	77-3990
Sulphate	2-1650
Sulphide	10
Total polar compounds	9.7-600
Higher acids	1-63
Phenols	0.009-23
Calcium	13-25800
Sodium	132-97000
Potassium	24-4300
Magnesium	8-6000
Iron	<0.1-100
Aluminium	310-410
Boron	5-95
Barium	1.3-650
Cadmium	<0.005-0.2
Chromium	0.02-1.1
Copper	<0.002-1.5
Lithium	3-50
Manganese	<0.004-175
Lead	0.002-8.8
Strontium	0.002-1000
Titanium	<0.01-0.7
Zinc	0.01-35
Arsenic	0.005-0.3
Mercury	<0.001-0.002
Silver	<0.001-0.15
Beryllium	<0.001-0.004

3. Produced brine treatment technologies

The treatment of wastewater includes physical, chemical and biological methods. Physical methods include gravity separation, adsorption, the use of hydrocyclone separators and techniques based on membrane filtration. Methods such as coagulation, flocculation and advanced oxidation processes, ion exchange and electrochemical processes belong to the chemical methods, while conventional activated sludge processes, solids reactors, membrane bioreactors and constructed wetlands belong to the biological methods (**Figure 3; Al Ghouti et al., 2019; Sahu, 2021).**

The selection of a suitable method is usually a challenge that is orientated towards costs and the goals of technical efficiency. To achieve these goals, a combination of different technologies is used to remove different components (**Figure 3**). The specific combination of these treatment methods depends on the characteristics of the produced water, regulatory requirements and the intended use. The impurities removed are categorised as Total Suspended Solids (TSS), organic compounds (such as phenols, Benzene, Toluene, Ethylbenzene and Xylen (BTEX), Polycyclic aromatic Hydrocarbons (PAHs)) and dissolved inorganic compounds, including heavy metals (**Arthur et al., 2005; Amakiri et al., 2022**).

METHOD	**1**	**2**	**3**	**4**	**5**	**6**	**1. De-oiling** **2. Suspended particles removal** **3. Iron removal** **4. Softening** **5. Soluble trace/organics removal** **6. Desalting**
API separator	■	■					
Deep bed filter	■	■					
Hydro cyclone	■	■					
Aeration and sedimentation		■					
Precipitation		■	■	■			
Ion exchange			■				
Biological treatment					■		
Thermal desalinisation		■		■		■	
Activated carbon	■		■	■	■		
Chemical treatment	■				■		
Ultrafiltration	■	■			■		
Nanofiltration	■	■	■	■	■	■	
Reverse osmosis	■	■	■	■	■	■	
Electrodialysis			■	■		■	

Figure 3: Technologies for specific components removal (according to **Nasiri & Jafari, 2017**)

All technologies can be categorised into primary, secondary and tertiary treatment (**Arthur et al., 2005; Amakiri et al., 2022**). By primary treatment oil droplets and suspended particles in the range of 5 to 15 µm are removed (hydrocyclone, API (American Petroleum Institute) separator, coagulation and flocculation). Adsorption, biodegradation, stripping and membrane separation are used to remove dissolved aromatic hydrocarbons such as BTEX. About 90 % of the oil droplets and soluble organic substances that have left the first treatment stage are removed in the second treatment stage (adsorption, activated sludge process, flotation). If required, the secondary effluent can be further treated by several tertiary processes (e.g. Advance Oxidation Process (AOP), electrodialysis). Tertiary treatment, known as final polishing, is used to remove dissolved solids, gases and dispersed hydrocarbons and focuses on the removal of salts from the treated production water. The tertiary treatment stages are used to remove other ultra-small oil droplets and other contaminants such as aromatic hydrocarbons (PAHs) (**Amakiri et al., 2022; Salem & Thiemann, 2022**).

Most of the methods-analysed in detail in the literature (adsorption, membrane filtration, activated sludge) have removal efficiency of over 90%. Reverse Osmosis (RO) globally appears to be the most commonly used desalination technology (**Randy & Inambao, 2019**). There are some new technologies that enable high water recovery of 90–98, e.g. Forward Osmosis (FO), Membrane Distillation (MD), Membrane Crystallisation (MCr), Electrodialysis (ED), Electrodialysis Reversal (EDR), Capacitive Deionisation (CDI), Eutectic Freeze Crystallisation (EFC) and Advanced Oxidation Processes (AOP). The extraction of organic pollutants from saline wastewater has already been analysed (**Lefebvre & Moletta 2006; Xiang et al. 2019**). Anaerobic/aerobic biological treatment and AOP have been shown to be viable for removing carbonaceous, nitrogenous and phosphorus contaminants at high salinity concentrations (**Sahu, 2021**). Theoretically, desalination of 1 m^3 of salt water requires around 0.86 kWh of energy, but the practical figures are 5 to 26 times higher than the theoretical minimum (**https://www.desware.net/**).

Several treatment systems are generally used in series. Which technology is most suitable depends on various conditions, e.g. the composition of the wastewater, the legal requirements, the overall costs, the by-products produced, etc.

4. Water electrolysis

In electrolysis, H_2O is converted to H_2 and O_2 using an external power supply to drive the oxidation of water at the anode and the reduction of water at the cathode, as in the following half-reactions (**Eq. 1-2**) (**Marouani et al., 2023**):

- Anode: $H_2O(l) \rightarrow \frac{1}{2} O_2(g) + 2H^+(aq) + 2e^-$ (1)
- Cathode: $2H_2(l) + 2e^- \rightarrow H_2(g)$ (2)

Eq. 1 refers to the Hydrogen Evolution Reaction (HER), and **Eq. 2.** to the Oxygen Evolution Reaction (OER).The amount of energy (nFE) required at equilibrium for splitting water molecules (1 mole of water) corresponds to the Gibbs free energy change (ΔGd) of the water dissociation reaction (**Eq. 3; Millet, 2015**):

- $\Delta Gd - n *x F x *E = 0; \Delta Gd > 0$ (3)

Where are:
ΔGd - free energy change (J/mol);
n - number of electrons exchanged during the electrochemical splitting of 1 water molecule (2);
F - Faraday constant (electric charge of 1 mole of electrons, approx. 96485 C/mol);
E - free energy electrolysis voltage (volts).

There are several organisations that have defined quality standards for the electrolysis inlet water, e.g. American Society for Testing and Materials (ASTM D1193 2011) or International Organisation for Standardisation (ISO 3696). The American Society for Testing and Materials classifies four different categories of water by quality (**Table 3**), with the Type 1 (of the highest quality) being used for electrolysers. A water treatment plant (WTP) is therefore required, the treatment process of which depends on the quality of the supply water (***https://jhuesa.com/***).

Table 3: ASTM water quality chategories (***https://jhuesa.com/***)

PARAMETER	Type I	Type II	Type III	Type IV
Max el. conductivity (µS/cm at 25 °C)	0.056	1	4	5
Max el. resistivity (MΩ m at 25 °C)	18.2	1	0.25	0.2
pH (at 25 °C)	--	-	-	5.0-8.0
TOC max (µg/l)	10	50	200	Unlimited
Sodium max (µg/l)	1	5	10	50
Silica max (µg/l)	33	3	500	Unlimited
Chlorine max (µg/l)	1	5	10	50

Theoretically the use of 9 m^3 of ultrapure water can lead to 1 kg of H_2, and in practice over 11 m^3 is required (**Simoes et al., 2021**).

5. Case study: potential of produced formation water from the hydrocarbon fields of the Drava Depression for H_2 production by electroliysis

In the case study, the formation water from seven (7) hydrocarbon fields located in Eastern part of the Drava Depression in the Croatian part of the Pannonian Basin System was analysed. After separation during the treatment and processing of formation fluid, the water is now disposed of by reinjection into deep wells. Instead of disposal, this paper analyses the potential of utilising this water for the production of green hydrogen.

The geotectonic position of the Drava Depression (red) within the Pannonian Basin System and area that approximately covers the Drava Depression are shown in **Figures 4** and **5**.

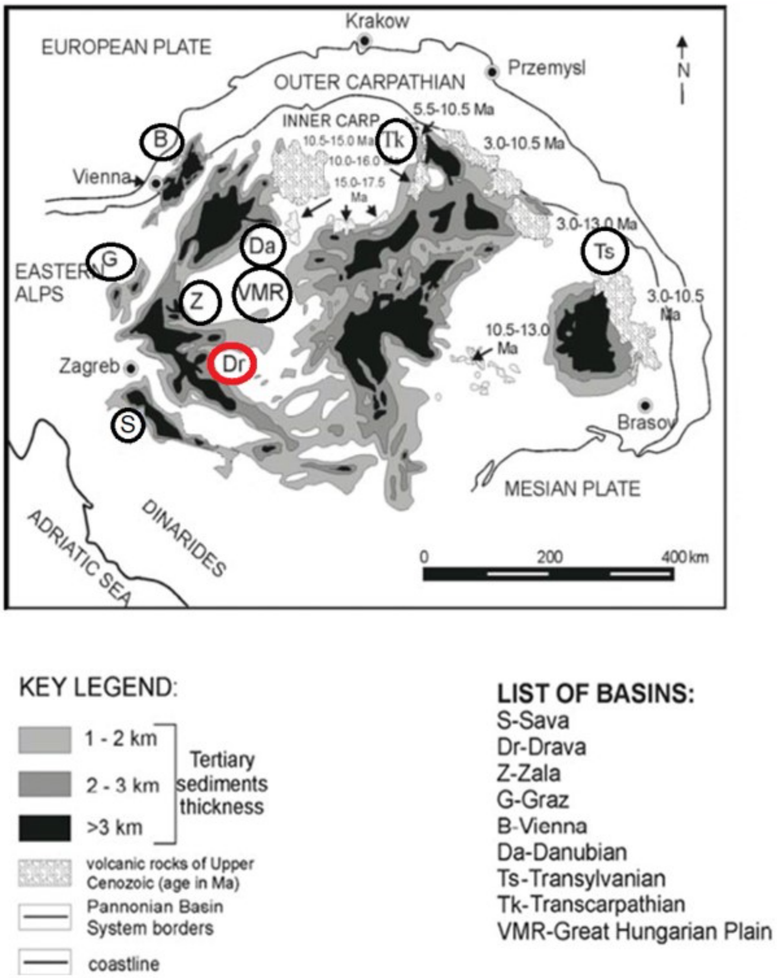


Figure 4: The geotectonic position of the Drava Depression within the Pannonian Basin System (**Malvić & Rusan, 2009**; **Ivšinović, 2017**)

Figure 5: Area that approximately covers the Drava Depression (**Malvić & Cvetković, 2013**)

The stratigraphic relationships in the subsurface of the eastern part of the Drava Depression are defined by lithostratigraphic units. The formations are defined by EK markers, which are characterised by clear recognisability and correlative properties due to their low thickness and large lateral extent, or by EK benchmarks, which in this case represents a discordance between younger Neogene-Quaternary and older magmatic-metamorphic-sedimentary rocks. **Figure 6** shows a schematic stratigraphic column of the Drava Depression (Croatian Western, Eastern and Hungarian parts).

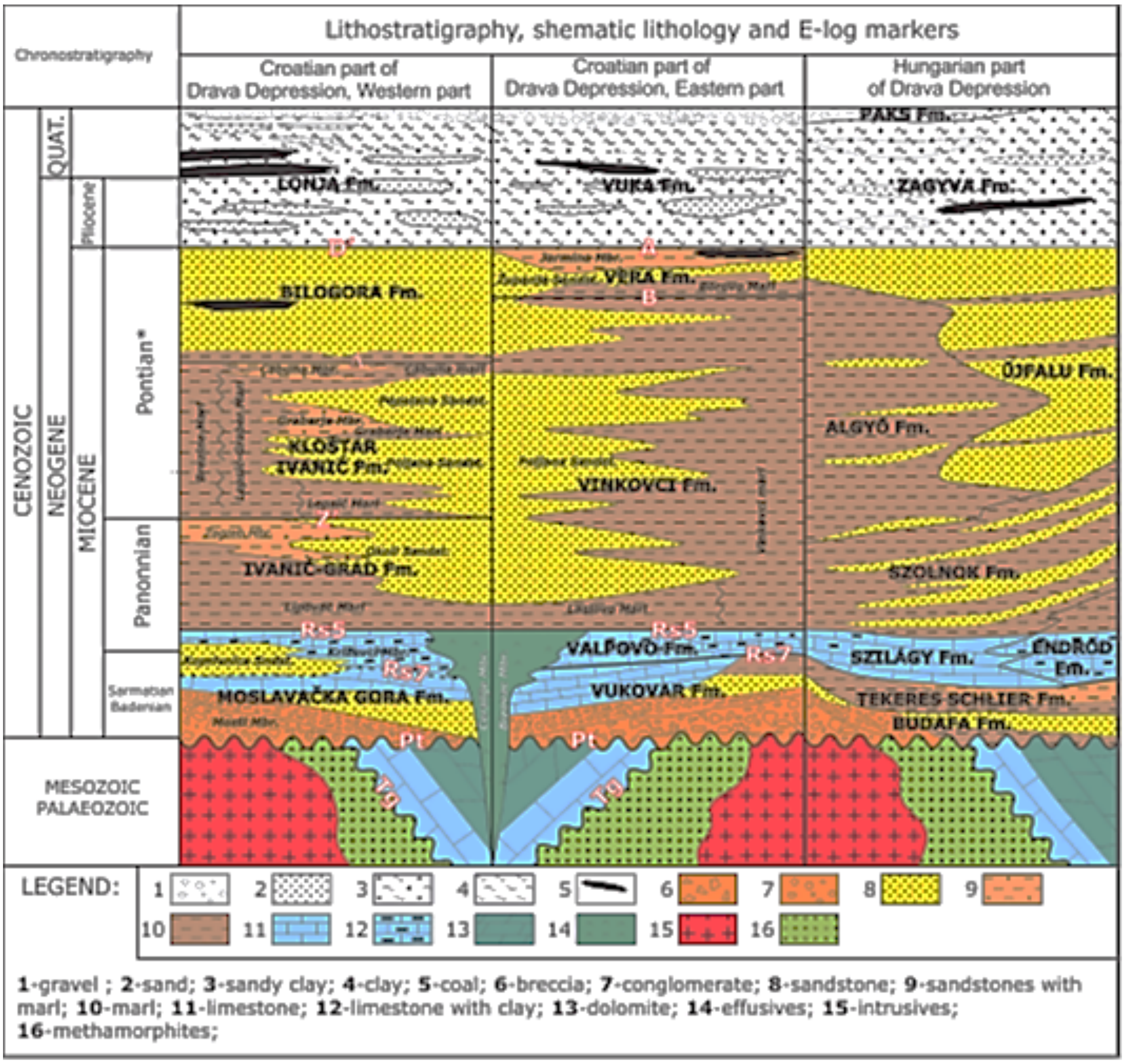


Figure 6: Lithostratigrphic column of the Drava Depression (**Malvić & Cvetković, 2013**)

A brief description of the existing gathering system of the oil fields under consideration is given further in the text. Fluid produced from the oil field "A" by flowing production or by gas lift, is trasported through flowlines to one of the three existing measuring stations (MS-1, MS-2, MS-3). The fluid produced from the field "B" by gas lift is transported through flowlines to the collector and further by the gathering pipeline to the collecting separator at the Oil Processing Plant (OPP). From the oil production fields "C" and "D" and "E", fluid is produced by using sucker road pumps and transported via flowlines to the collector and further via gathering lines to the collecting separator in the OPP. Well-production fluid from the hydrocarbon fields "E", "F" and "G" is carried by flowlines to the MS 4 and further to OPP (**INA d.d., 2017**).

At the measuring stations, the liquid is separated from the gas, the liquid and gas volumes are measured and then the fluids are transported separately to OPP site. The gas collected from the measuring stations is transported from the OPP through the gas pipeline to the consumer, while the liquid (mixture of oil and water) is transported to the heat exchangers in the OPP. From the heat exchanger, the liquid is channelled into the gun-barrel. The separated water is extracted and passes into the decanter and then through the waste water separator into brine tank. The brine is then pumped from the tank to the injection wells.

The oil is transported from the dehydrator to the dry oil tank. The dehydrated (dry) oil from the process tanks is then transferred to the 5 000 m^3 dry oil tanks (R-5000). Gravity separation is used to separate an additional quantity of water in the R-5000, which is pumped into the injection wells together with the remaining water separated during oil processing. The water injection is only used for disposal, not for pressure maintenance (**INA d.d., 2017**).

Annually almost 500 000 m^3 of formation water is produced and reinjected (**INA Group, 2020**). The average content of produced formation water is given in **Table 4**. The quantities of water produced and re-injected underground are shown in **Figure 7.**

Table 4: The average content of formation water processed at OPP

PARAMETER	VALUE	PARAMETER	VALUE
pH	6.8	Fe^{2-}(mg/l)	-
Max el. conductivity (µS/cm at 25 °C)	1803	Fe (mg/l)	0.632
Max el. resistivity (MΩ m at 25 °C)	0.555	Cl$^-$ (mg/l)	5424.3
Density (kg/dm^3)	10086	CO$_3^{2-}$(mg/l)	-
Suspended solids (mg/l)	43	HCO$_3^-$ (mg/l)	1792
NH$_4^-$ (mg/l)	26.3	SO$_4^{2-}$ (mg/l)	51
Na (mg/l)	3860	Salinity (gNaCL/l)	8.94
K (mg/l)	86.4	H$_2$S (mg/l)	8.7
Mg (mg/l)	69	CO$_2$ (mg/l)	440.5
Ca (mg/l)	177.3	Br- (mg/l)	28
Sr (mg/l)	17.2	TOC (No/ml)	48.3

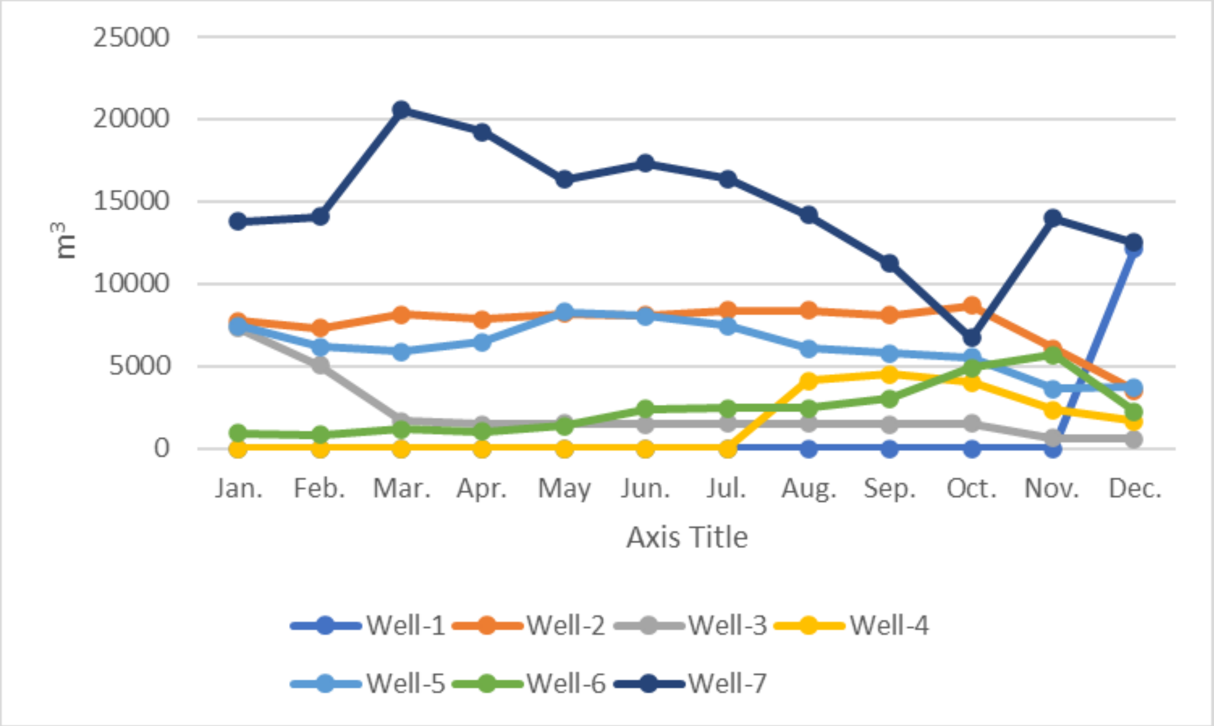


Figure 7: Quantities of brine reinjected

5.1. Calculation of the hydrogen production potential from brine and required energy

The total volume of production water to be disposed of within a year can be estimated at approx. 500 000 m³. If the entire water production to hydrogen takes place by means of electrolysis plants, the amount of electrical energy that would have to be available to the electrolysis plants must be calculated. The amount of produced H_2 can be calculated using the following equations, which are based on Faraday's laws of electrolysis:

1. Total electric charge (Q):

- Q = I x t (4)

Where are:

Q - total electric charge (C)
I - electric current (A)
T - time of electrolysis (s)

2. Mass of produced H_2:

- m = (M x Q) / (n x F) (5)

Where are:

m - mass (g)
M - molar mass (approx. 2 g/mol for H_2)
n - number of electrons required (2 for H_2)
F - Faraday's constant (approx. 96485 C/mol)

3. Volume of hydrogen (V) produced at standard conditions:

$$V = (Q \times V_m) / (n \times F) \quad (6)$$

Where are:

V - volume of hydrogen (l)
V_m - molar volume of gas at standard conditions (approx. 22.4 l/mol)

For calculation of the required energy for electrolysis **(Eq. 9)**, total number of moles of hydrogen **(Eq. 7-8)** is required, as follows:

- **Calculation of the number of moles of water**
  Water mass = 500 000 000 kg (water density = approx. 1 kg/l)
  Moles of water = $\frac{500\ 000\ 000\ kg}{0{,}018\ kg/mol} \approx 27\ 777\ 777\ 778$ mol (7)

- **Calculation of moles of hydrogen:**
  Each mole of water (H_2O) yields 1 mole of O_2 and 2 moles of H_2.
  Total number of moles of hydrogen = 2 x 27 777 777 778= (8)
  = 55 555 555 556 mol

- **Calculation of the required energy for electrolysis:**

According to Faraday's law of electrolysis, producing 1 mole of hydrogen requires approximately 237 kJ of electrical energy. Total required energy is calculated according to **Eq. 9-10:**

Total required energy = 55 555 555 556 * 237 =13166666666772 kJ (9)
≈13 167 000 000 MJ

Expressed in MWh (1 kWh = 3600 kJ):

$$\text{Total Energy} = \frac{13166666666772\ \mathrm{kJ}}{3600\ kj/kWh} \approx 3\ 657\ 407,\ 407\ \mathrm{MWh} \tag{10}$$

Using the basic expression for calculating power, the required power of the electrolyser system amounts to **(Eq. 11)**:

- $$\mathrm{P}= \frac{3{,}657{,}407{,}407\ \mathrm{kWh}}{8760h} = 417\ 661\ \mathrm{kWh} \approx 418\ \mathrm{MW} \tag{11}$$

The PEM (Proton Exchange Membrane) electrolysers from Siemens, in particular the Silyzer 300 model, are known for their high efficiency and performance in hydrogen production. The efficiency of these systems is between 75 % and 80 %, which is quite high for electrolysis technology. In terms of the specific energy required to produce hydrogen, Siemens electrolysers generally require around 60 kWh of electricity to produce one kilogramme of hydrogen. With an electrolyser output of 418 MW and continuous operation over a period of one year, around 61 000 t of H_2 could be produced. **Figure 8** shows the calculated H_2 volumes, and the electrical energy required per volume of water quantities injected underground, expressed by each well.

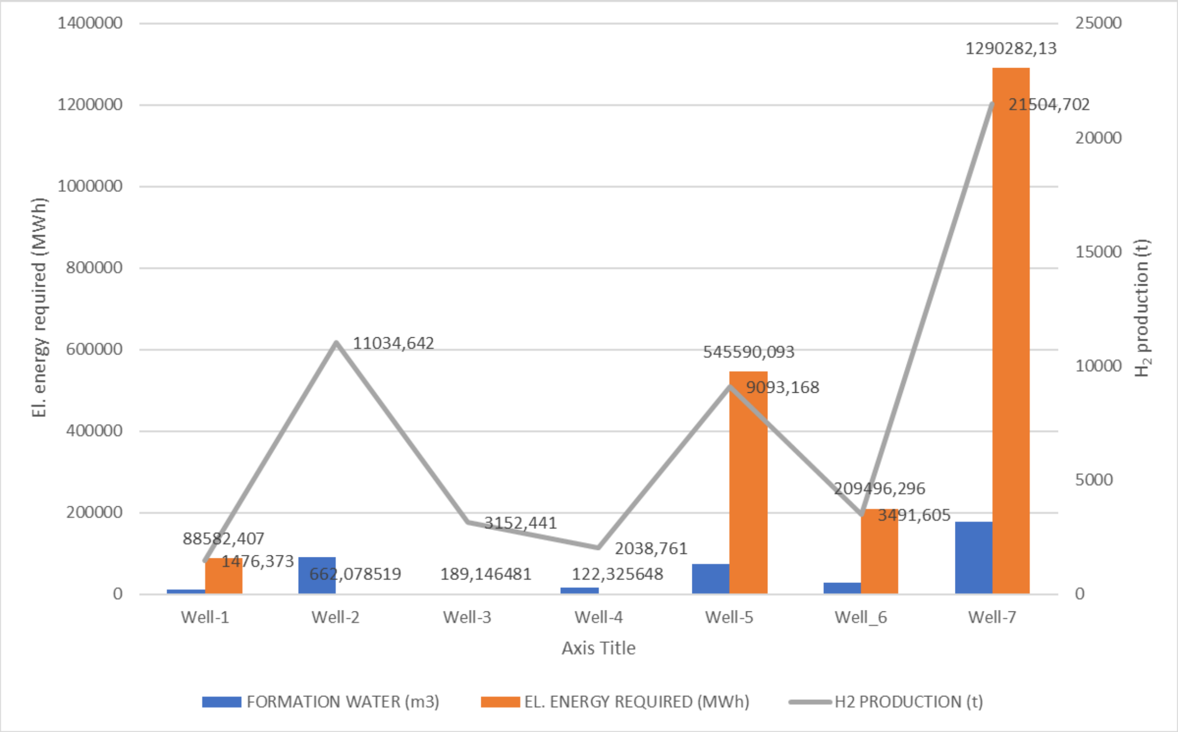


Figure 8: H_2 production and electrical energy required for the quantities of water currently injected by the well

6. Discussion

The EU climate target of decarbonisation by 2050 envisages a share of at least 13% hydrogen in the energy mix by 2050, which is feasible with the installation of 40 GW of renewable hydrogen electrolysers by 2050 (**EC, 2020).** Technological improvements being developed in various scientific fields with the aim of cost efficiency are crucial. The production of hydrogen from formation water by electrolysis using green electrical energy would be a good example of the circular economy concept. To achieve commercialisation, many obstacles to existing technologies need to be overcome.

Alkaline water electrolysis is the current technology for large-scale electrolytic hydrogen production. It is characterised by low efficiency, low current density and the lack of suitable scale-up practise. Since high-quality water is used for electrolysis, additional purification pre-treatment is required, which increases the cost of such a project (**Abdel-Aal et al., 2010**). **Nasiri & Jafari (2017)** analysed different methods of produced water treatment along with challenges and opportunities of each of them. When saline water is used as an inlet, the required ASTM Type I water quality can be achieved using commercially available reverse osmosis and deionisation systems. Nevertheless, the question of the energy consumption of WTP is often raised, especially when it comes to water desalination. However, it must be emphasised that the attractive forces between water molecules and ions must be overcome during water treatment, while at the same time the strong covalent bonds between the atoms in the water molecules must be overcome during electrolysis (***https://hydrogentechworld.com/***).

While the treatment of fresh groundwater involves pre-treatment by sand filtration and aeration, saltwater must be desalinated. Softening, degassing, demineralisation and polishing are required to obtain pure water. In electrolysis systems such as Proton Exchange Membrane (PEM) and Anion Exchange Membrane (AEM), which work with ultrapure water, the water entering the electrolysis system is continuously contaminated with metal ions from the pipes and process equipment as well as with ions and organic substances from the electrolyser stack. Due to extension of the electrolyser lifetime, such components are being removed with the aid of side stream polishers (**Farràs et al., 2021; https://www.eurowater.com/).**

Theoretically, 39.4 kWh, but taking into account various inefficiencies, water electrolysis requires an average of 50 – 55 kWh/kg. The most commonly used reverse osmosis systems consume an average of 0.0012 kWh/l of brackish water or 0.0046 kWh/l of seawater as feedstock. If a system for treating demineralised water is also used to meet the required quality standards, the energy consumption increases by around 0.0016 kWh/l. The total energy consumption for treatment is about 0.055 to 0.077 kWh/kg of H_2, which is less than 0.2% of the total energy consumption for hydrogen production. Innovative reverse osmosis and demineralisation plants are cost-efficient, so that the total costs for water desalination can be reduced to around 0.85 USD/m^3 (***https://www.weforum.org/***).

As presented in previous chapter, to convert 500 000 m^3 of produced water (treated up to the level of pure water) into chemical energy of hydrogen by electrolysis, a total of 3.7 TWh of electrical energy is required over the course of one year.– With a 418 MW electrolyser in continuous operation over a period of one year, around 61 000 t of H_2 could be produced. Considering that the current hydrogen demand in Europe is 8.7 million tonnes (Mt) per year (grey hydrogen), as well as the EU's ambitious target of producing 10 Mt of renewable hydrogen and importing 10 Mt of renewable hydrogen by 2030 (**EC, 2020**), it is obvious that only a small proportion of the produced formation water from the fields considered in this work could be realised in hydrogen production.

As already mentioned, another way to utilize brine for electrolysis is to develop an electrolysis system that can utilise seawater for direct electrolysis. It is likely that these systems would operate at a low power density and would only electrolyse a small proportion of the water in contact with the electrodes.

In addition to the potential advantages in terms of reusing of the produced water, which is actually waste, there are many disadvantages resulting from the lack of technology to overcome corrosion and contamination problems and the development of undesirable electrochemical products such as chlorine. Due to the low conductivity of brine, the sluggish HER kinetics require a high conductivity electrolysis catalyst to enable rapid charge transfer, which represents the first problem. The second problem is the presence of bacteria and microbes in the seawater and the resulting formation of insoluble deposits on the catalyst surface, and the third issue is the corrosiveness of brine, which negatively affects most metal-containing catalysts. Since the same current surge that is responsible for O_2 generation at the anode also converts the chloride ions in the brine into highly corrosive chlorine gas that corrodes the electrodes and catalysts, this causes the electrolysers to fail immediately within a few hours (normally they can function for years). Such major obstacles have resulted with small progress made so far (**Alasali et al., 2024; Huang**

et al., 2024; Kasani et al., 2024; Shi et al., 2024; Sun et al., 2024; Wang et al., 2024; ***https://www.science.org/*).**

The cell for freshwater electrolysis is known as an H_2/O_2 cell, while the cell for saturated brine behaves more like an H_2/Cl_2, which is responsible for caustic soda production. In the H_2/O_2 cell, hydrogen/oxygen is produced in a ratio of 2:1, while in the H_2/Cl_2 cell hydrogen/chlorine is produced in a molar ratio of 1:1, which means that the hydroxide ions migrate to the anode (positive electrode) where oxidation takes place, but there is competition between the hydroxide ions and the chloride ions to be oxidised. In the electrolysis of a sodium chloride solution, four products therefore appear to be possible (sodium, chlorine, hydrogen and oxygen). It is worth to note that the sodium is extremely reactive and therefore reacts immediately with water, producing sodium hydroxide (NaOH)(aq) (***https://www.nagwa.com/***). However, the overall process is given by the **Eq. 12 – 14**.

$$2NaCl+2e^- = 2Na + Cl_2 \qquad (12)$$

$$2Na+2HOH = 2NaOH + H_2 \qquad (13)$$

$$2Cl = Cl_2 + 2e^- \qquad (14)$$

The use of oxygen-selective electrodes seems to be the most promising way for the electrolysis of brine. The oxygen reaction is more dependent on the electrode material than the chlorine reaction, and at low overpotential with different electrode materials (manganese or MnO_2), at a pH value of 0-3, the reaction potential of O_2 is higher than that of Cl_2 (**Abdel-Aal et al., 2010**).

Furthermore, in terms of its contents, seawater is much less complex than average oil-fields produced water (**Shaddel & Tabatabae-Nejad, 2014**). It is therefore obvious that one line of further research and technology development would lead to improving the efficiency and cost of both water treatment methods, while another line of research would cover the issue of direct utilisation of produced formation water in electrolysis.

7. Conclusion

While reinjecting produced water into wells for reservoir pressure maintenance or permanent disposal remains the predominant commercial method for brine management, modern circular economy models emphasis using resources for as long as possible. This approach opens up alternative uses for produced water, aligning with environmental goals by reducing freshwater consumption.

However, the suitability of formation water for electrolysis depends on factors such as its composition and the required purity. The purity of Type 1 water is crucial for achieving high hydrogen production efficiency and preventing the degradation of electrolysis components. Depending on the specific composition of formation water, treatments such as reverse osmosis and deionization are necessary.

The various electrolysis technologies have varying tolerance levels for impurities in the water feedstock. Electrolysers for direct usage of formation water are under development, but significant issues like corrosion, contamination, and the development of undesirable electrochemical products such as chlorine need to be addressed.

Both the hydrogen economy and water electrolysis are well-established concepts, but currently, green hydrogen is generally not cost-effective compared to hydrogen produced from fossil fuels (grey hydrogen), due to the high cost of electrolysis and expensive renewable energy. However, there is significant potential for cost reductions in the future. Technological advancements, economies of scale, and supportive government policies could all contribute to lowering the cost of green hydrogen.

Although the total power of the electrolysis system of 418 MW calculated in this study seems technically very demanding, the continuous increase in the share of renewable energy sources (wind farms and solar systems) in Croatia, the limitations of the electrical energy infrastructure, and the increasingly problematic ability to balance the electrical energy system necessitate the construction of infrastructure capable of performing energy balancing with larger capacities. The conversion of part of the produced water into hydrogen by utilizing excess electricity from the grid, rather than its disposal, might prove economically viable upon further techno-economic analyses, especially when considering the permanence of the constructed infrastructure and the possibility of expanding the electrolyser capacities depending on the availability of electrical energy.

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SAŽETAK

Pristup kružnog gospodarstva kod proizvedene slojne vodi: mogućnosti i izazovi

Procesi eksploatacije nafte i plina generiraju i slojnu vodu čija se količina povećava s vremenom, pa postupanje s istom postaje sve veći problem. U skladu s konceptom kružnog gospodarstva, a s ciljem smanjenja potrošnja svježe vode, razmatraju se alternativne mogućnosti upotrebe slojne vode. Jednu od takvih mogućnosti predstavlja iskorištavanje slojne vode za proizvodnju zelenog vodika u elektrolizatorima. Za elektrolizu potrebna je voda visoke čistoće kojom se osigurava učinkovitost i dugovječnost sustava, zbog čega su potrebni procesi obrade. Izravna uporaba slojne vode povezana je s problemima, kao što su korozija i onečišćenje opreme. U radu su analizirane količine slojne vode proizvedene u sastavu ležišnog fluida, tijekom eksploatacije nafte i plina u istočnom dijelu Dravske depresije, a koje se trenutno utiskuju u ležišta radi deponiranja. Iako model koji uključuje snagu sustava za elektrolizu od 418 MW, a kojim bi se iskorištavala sva proizvedena slojna voda, predstavlja izazov, model kojim bi se iskorištavao dio slojne vode i koristio višak električne energije za pretvaranje iste u vodik, mogao bi biti održiva opcija.

Ključne riječi: slojna voda; Dravska depresija; eksploatacija ugljikovodika; vodik; elektroliza, kružna ekonomija.

Authors contribution

Karolina Novak Mavar: provided the methodology and elaboration of the initial design; provided final concept, discussion and conclusion; **Ivan Zelenika:** provided the calculations for the case study; reviewed and supervised the work; **Katarina Simon**: provided the brine treatment technologies and gave a brief description of the existing gathering system of the considered oil fields; reviewed and supervised the work.