Seawater Refinary: A Pathway for Sustainable Metal Recovery and Green Hydrogen Production

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With the growing environmental challenges of saltwater desalination, seawater mining is emerging as a sustainable alternative to traditional onshore mining. This paper explores the potential of recovering metals from seawater and producing green hydrogen, proposing a "seawater refinery" concept inspired by oil and biorefineries. The refinery leverages advanced separation technologies and "Zero Liquid Discharge" methods to convert brine into valuable products, including green hydrogen (H_2) while minimizing environmental impacts.

Keywords: Desalination. Metal Recovery. Membrane Processes. Green Hydrogen.

The global shift toward a hydrogen-based economy, coupled with carbon dioxide (CO_2) capture technologies, offers a promising pathway for decarbonizing industrial sectors. However, the increasing demand for hydrogen (H_2) could exacerbate water consumption, raising concerns about competition with potable water supplies essential for human and environmental needs [1,2].

Seawater has been identified as a viable water source for H_2 production, provided it undergoes desalination before electrolysis. However, desalination processes generate brine discharge with detrimental environmental impacts. This waste contains elevated salinity levels, heavy metals, and residues of chemical additives used during desalination, such as anti-scaling, anti-foaming, and anti-corrosion agents. Discharge affects local ecosystems by altering the receiving environment's physicochemical properties, including temperature, turbidity, and dissolved oxygen levels. These changes adversely affect biodiversity, metabolic rates, and the physiological health of marine life [3,4].

In parallel, the global demand for rare and valuable metals has heightened interest in sustainable extraction methods. Seawater mining presents a compelling alternative, mainly through brine concentrate mining, which offers energy-efficient and environmentally friendly means to extract valuable metals like magnesium (Mg), lithium (Li), uranium (U), potassium (K), and sodium (Na). These elements are crucial in energy storage, transportation, agriculture, and electronics [5,6].

Inspired by the operational principles of oil and biorefineries, this paper introduces the concept of a "seawater refinery." This approach focuses on maximizing resource efficiency and minimizing waste by separating various valuable products—including metals, green H_2, and chemicals—directly from seawater.

Materials and Methods

The method for this study involved a detailed and systematic approach to explore the feasibility of a seawater refinery for metal recovery and green hydrogen (H_2) production. Key steps are outlined below:

Comprehensive Literature Review

A thorough review of existing literature was conducted, focusing on:

- Mining and recovery of metals from brine.
- Desalination technologies specific to seawater.

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- Water consumption during the electrolysis process for H_2 production.

The Web of Science database was used as the primary search platform to gather relevant literature. Additionally, the snowballing method was applied, employing two complementary approaches:

- Backward snowballing: Analyzing the reference lists of selected papers.
- Forward snowballing: Review articles that cited the primary papers.

Suggestions from journal recommendation algorithms were also incorporated to ensure a well-rounded collection of resources.

Synthesis of Information

Data and insights from the literature were synthesized to comprehensively understand the potential for adding value to brine.

Brine, a byproduct of desalination, presents environmental challenges and contains valuable resources that can be recovered.

Process Flowsheet Development

Based on the synthesized information, a conceptual process flowsheet for the seawater refinery was developed. The flowsheet outlines the main stages of resource recovery and green H_2 production.

Assessment of Technological Feasibility

The complexity and readiness of the proposed refinery were evaluated using Technology Readiness Levels (TRLs) and Manufacturing Readiness Levels (MRLs):

- TRLs: Represent the maturity levels of tangible technologies involved in the refinery processes.
- MRLs: Denote the maturity levels of production processes (intangible assets) required to implement the refinery.

Table 1 presents the TRL and MRL classifications, providing insights into technological development and production readiness. This dual assessment approach ensures that the seawater refinery's technological and operational aspects are critically evaluated for feasibility and scalability [7].

This structured method ensures that the study addresses both the theoretical and practical dimensions of the seawater refinery concept, paving the way for its potential implementation.

Results and Discussion

Challenges in Conventional Mining

Traditional mining practices face numerous difficulties, including:

- Depletion of high-grade ores: Resources of superior quality are becoming scarce, making extraction increasingly uneconomical
- Rising environmental costs: Managing the ecological impact of mining has become costly.
- Reduced ore quality: Available reserves often consist of lower-quality ores, further complicating extraction processes.
- Stricter regulations: Environmental policies are becoming progressively stringent, adding compliance challenges.

Given these constraints, metal recovery from seawater presents an innovative and sustainable alternative, reducing dependence on terrestrial mining while tapping into an underutilized resource.

Historical Context of Seawater Mining

The idea of extracting valuable components from desalination concentrate dates back to Dr. John F. Mero in 1964. He predicted that desalination brine could play a pivotal role in

Table 1. TRLs and MRLs levels for complexity assessment [7].

Level Definition	TRL	MRL
Ideation	This is the lowest level, where the technology is still in the theoretical or conceptual stage, and there is no experimental evidence or proof of concept.	The manufacturing process is still in the early conceptual stage, and basic principles are being explored.
Conception	At this level, the technology concept is defined, and there might be some initial experimental evidence to support its feasibility.	The manufacturing concept is defined, and initial analyses are conducted.
Proof of concept	The technology is now proven to work in a laboratory environment or through analytical studies, demonstrating its feasibility	The process is proven to be feasible through studies and experiments.
Otimization	A prototype of the technology is built and tested in a controlled laboratory setting, showing its potential functionality.	The process is demonstrated in a laboratory setting.
Prototyping	The technology's prototype is tested in a relevant environment that simulates realworld conditions, confirming its performance capabilities.	Process is validated in a relevant environment.
Escalonation	A more advanced prototype is tested and demonstrated in an actual operational environment.	A prototype manufacturing system is tested in a productionlike environment.
Demonstration in operational environment	At this stage, a system prototype is tested and proven to work in an operational setting.	The prototype manufacturing system is demonstrated in a relevant operational environment.
Production	The technology is now fully developed, and it has undergone rigorous testing to ensure it meets the required specifications.	A pilot manufacturing system is fully operational and represents a near-final design.
Continued production	The technology has been successfully deployed and used in real missions or operational scenarios.	The manufacturing process is fully matured and ready for fullscale production.

future mineral production from seawater. This concept gained renewed attention in 1994 through the work of Petersen, inspiring several subsequent research efforts to develop viable extraction methods [6,8,9].

Brine Mining Technologies

The development of brine mining technologies, particularly advancements in membrane-based separation processes, has dramatically enhanced the feasibility of extracting metals from desalination concentrate.

Desalination Technologies

Desalination methods are categorized into conventional and emerging technologies based on their maturity and market presence. Conventional methods like:

- Reverse Osmosis (RO)
- Nanofiltration (NF)
- Electrodialysis (ED)

have significantly reduced operational costs. For example, the cost of seawater desalination has decreased from US\$10.00/m³ in the 1970s to US\$0.15/m³ by 2021 [10], making it a more economically viable option. Emerging technologies are described as innovative approaches with the potential to enhance recovery efficiency and sustainability.

Economic Viability of Metal Recovery

The recovery of metals such as Na, Ca, Mg, K, Li, Sr, Br, B, and U from seawater is deemed feasible under certain economic conditions. Loganathan and colleagues (2017) correlated the estimated quantities of these minerals in seawater with their terrestrial reserves (Figure 1).

For economic viability, the Market Price (Pm) of the metal must satisfy the following conditions:

$$P_m \geq \frac{POWCL}{C_m} \qquad (1)$$

Where: Pm = Market Price (Pm); LCOWP = Levelized Cost of Water Processing, and Cm = Metal Concentration [6,11-13].

Figures 1 and 2 illustrate: the recovery potential of various metals., and the economic thresholds for profitability in brine mining operations.

These results underscore the transformative potential of seawater refineries in addressing resource scarcity and promoting sustainability.

Kumar and colleagues (2019) discuss the direct electrosynthesis of NaOH and HCl from seawater desalination brine, and water electrolysis is gaining momentum globally as a route to decarbonize our energy systems. Table 2 shows the most common minerals and chemicals potentially produced from seawater and its primary uses. The most common desalination system is based on RO and ED.

Membrane distillation (MD) is a standard process to recover Na, Ca, Mg, K, and the Adsorption/desorption process (ADSM) to recover Li, Sr, Br, B, and U Table 3 describes these treatment technologies and some other technologies required for metal recovery [3,6,12,13].

Figure 1. Estimated ratio of the amounts of minerals in oceans [6].

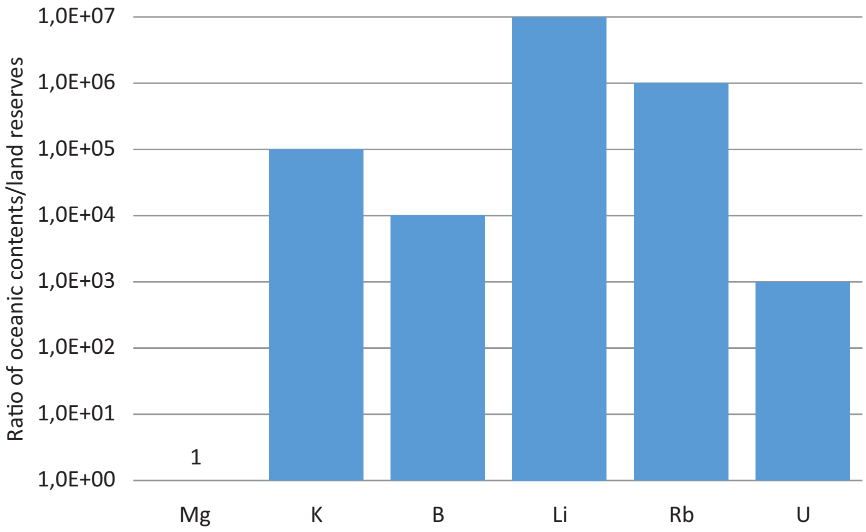
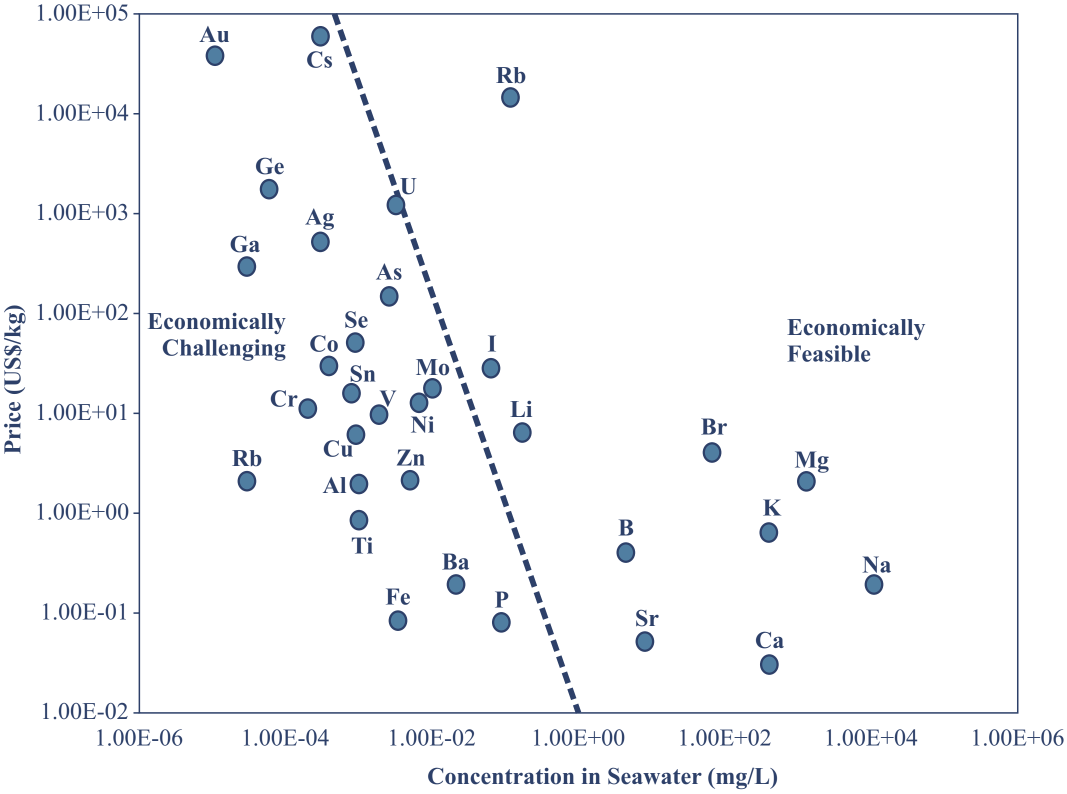


Figure 2. Minerals that can be economically extracted from seawater [6].



The technological advances of each method described in Table 3 demonstrate a promising potential for its application in mining seawater brine minerals. From bibliographical studies, using Table 3 and with the intention of recovering or producing the products listed in Table 1, Figure 3 presents the proposed flowchart for the seawater refinery. This refinery makes metal recovery economically viable from Loganathan (2017) (Figure 3) and produces green hydrogen through PEM electrolysis and chemicals through the chloralkaline process, using a membrane electrolyzer for this purpose.

Conclusion

The concept of a "Seawater Refinery" demonstrates promising technological and economic potential, as evidenced by the high Technology Readiness Levels (TRLs), which exceed 7 for its core processes. These levels indicate that many underlying technologies are mature and capable of operational deployment. However, the Manufacturing Readiness Levels (MRLs) for the seawater refinery are relatively low, currently around 3 or 4. This reflects the early stage of development, where the concept has been defined, and initial proof-of-concept work has been conducted. Further efforts are required to advance to higher MRLs, including piloting or full-scale demonstrations of the proposed refinery.

Future research directions should focus on mathematical modeling and process simulation, enabling an economical and environmental analysis by evaluating it though UN SDG and green engineering principles, or its environmental and social impacts using LCA approaces.

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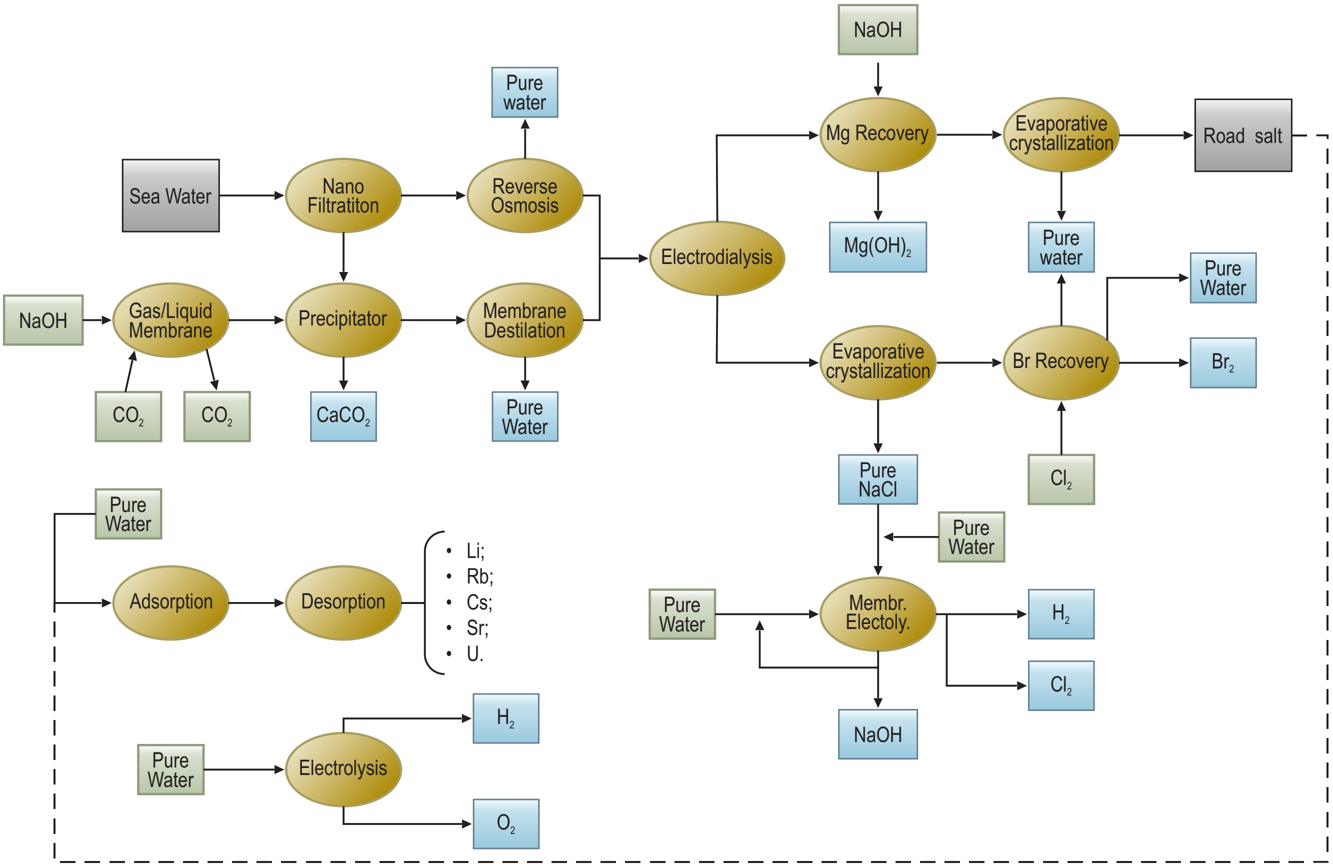
Table 2. Significant uses of valuable minerals and chemicals that can be economically mined from seawater.

Mineral	Major Uses
Na (NaCl, Na_2CO_3, Na_2SO_4)	Food, glass, soap, detergent, textiles, pulp and paper industries, road deicing.
Mg (Mg, $MgSO_4$, $MgCO_3$)	Steel, chemical and construction industries, fertilizer.
Ca ($CaCO_3$, $CaSO_4$)	Soil amendment, construction industries, fertilizer.
K (KCl, K2SO_4)	Fertilizer.
Br	Fire retardant, agriculture, well-drilling fluids, petroleum additives.
B	Glass products, soap and detergents, fire retardants, fertilizer.
Sr	Ceramics; glass, oil, gas and pyrotechnics industries; ceramic ferrite magnets; phosphorescent pigments; fluorescent lights.
Li	Batteries; glass manufacturing; lubricants and greases; pharmaceutical products.
Rb	Fibre optics; lamps; night vision devices; laser technology.
U	Nuclear fuel in nuclear power reactor.
NaOH	Used in the production of various chemicals like detergents; soaps; and paper; water/wastewater treatment; aluminum production.
HCl	Production of various chemicals; including hydrochlorides; metal pickling; pH adjustment; water treatment.
Cl_2	Widely used for water disinfection to kill bacteria and pathogens; PVC production; pulp and paper industry for bleaching wood pulp; synthesis of various chemicals, like hydrochloric acid.
H_2	Clean and renewable energy source for fuel cells and combustion engines; ammonia production; food industry for hydrogenation reactions (e.g., margarine production); hydrocracking process to produce high-quality fuels.
O_2	Used in respiratory support and medical gas therapies; combustion; metal cutting; welding and oxy-fuel combustions.

Table 3. Technology descriptions.

Treatment Technology	Synonyms	Description	TRL
Adsorptive Media	N/A	New materials used to remove pollutants via surface adhesion. Do not use this code for packed-bed or any granular-filtration process. Expect these to have copyrighted names. This code excludes GAC.	7
Electrodialysis	Electrodialysis Reversal (EDR)	Involves moving ions in a potential field across alternating polymeric anion- and cation-exchange membranes. A potential difference applied across the membranes traps ions and separates a brine waste stream from purified water. Electrodialysis works best for removing low molecular weight charged species.	8
Reverse Osmosis	Desalination	A membrane filtration method used to remove small ions (e.g., Na+) from water. Requires a high-pressure hydraulic pressure gradient to counteract the osmotic pressure gradient that would otherwise favor movement of water into (instead of out of) the concentrated wastewater or saltwater.	9
Nanofiltration	N/A	A membrane filtration method used to remove particles as small as 1 nm from wastewater. This includes divalent and large monovalent ions (e.g., heavy metals). Used for desalination and softening.	7
Membrane Distillation	N/A	A Hydrophobic membrane separates two aqueous solutions in a temperature-driven process. Water vapor passes through the membrane due to vapor pressure and condenses.	7
Evaporation	N/A	Water is vaporized, can be condensed for reuse, and leaves concentrated brine with dissolved solids. It occurs in solar evaporation ponds or with commercial equipment. Brine can be further concentrated during crystallization (CYS).	9
Crystallization	Fluidized Bed Crystallization	A Crystallization forms solid crystals from a solution, that can be applied post-evaporation for solid waste or product recovery. For recovery, it combines coagulation, flocculation, sludge/water separation, and dewatering, producing high-purity water.	7
Chemical Precipitation	Coagulation and Flocculation	A Chemical addition removes suspended solids from water. It neutralizes charged particles (coagulation) and promotes clump formation (flocculation), aiding settling. Additionally, it removes soluble metals through precipitants forming insoluble compounds.	8
Water Electrolyser	PEM electrolyser	Uses PEM to produce clean H_2 from water. Splitting the water into O2 and protons.	8
NaCl Electrolyser	Chlor Alkali electroyser	Utilizes electrolysis of NaCl solution to produce Cl2, NaOH, H2, essential for chemical manufacturing and water treatment.	9

Figure 3. Flowsheet for the seawater refinery.



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