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A New Disruptive Technology for Zero-Brine Discharge: Towards a Paradigm Shift

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Abstract: The desalination of aquifers and seawaters is a viable choice to meet primarily domestic and industrial global water requirements. It removes salts from seawater to obtain freshwater with sufficient quality for different purposes, as well as a highly salt-concentrated waste stream known as brine. This residue is usually returned to the ocean, provoking, among other impacts, changes in temperature, salinity and oxygen and overall local aquatic ecosystem stress, as well as social rejection. Desalination in inland aquifers is more complicated because brine disposal is complicated or impossible. The current study presents a new zero-brine discharge technology able to achieve ecological liquid purification through distillation for the separation of the dissolved solids as crystallized salts (Adiabatic Sonic Evaporation and Crystallization, ASE&C). This new technology was used with seawater and three types of brine to test how it would work when coupled with reverse osmosis desalination plants. Analysis of the byproducts after treatment of the seawater and the different brines are presented here. A basic economic approach to calculating potential revenues is also presented. The results of the analyses revealed a complete depuration of water as distilled water, and crystallized solids with highly concentrated commercial salts (with different composition depending on their origin). The estimated economic value of annual revenue (taking into account only seven element recoveries and treatment of a volume of 1000 m^3/d) for three types of brines ranged between 1 and 11 million euros, compared to between 3.6 and 9.3 million euros when ASE&C is employed with seawater. The treatment of greater volumes for seawater desalination would increase these numbers significantly. ASE&C supposes a solution coupled (or not) to desalination plants to reduce the ecological impacts associated with brine discharges to zero, obtaining two significant commercial byproducts: (seawater: freshwater and commercial elements Br, Ca, Cs, Cl, NaOH, Mg, N, K, Rb, Na, Sr, Li, U, B, Sr, Ga, etc.; aquifers: a larger list than for saltwater, depending on the nature of the water body). It can solve environmental issues associated with brine discharge, with null CO_2 emissions (renewable energy) and profitable (i.e., with no costly pretreatment) technology.

Keywords: desalination; seawater treatment; aquifer desalination; ASE&C; brine mining optimization; circular economy

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1. Introduction

Despite being called the Blue Planet because two thirds of it is covered by water, 97% of the water of the Earth is seawater (Figure 1a) and only 3% is freshwater, in the form of glaciers (2.5%) and other water bodies of groundwater (aquifers), superficial water (lakes and rivers), atmosphere (water vapor), and even organisms [1,2]. A combination of the exponentially rising population, the advance of drought and desertification as consequences of global warming and climate change, and the scarcity and unequal global distribution of water resources and other associated problems such as pollution is endangering, aggravating, and accelerating the loss of water available for human consumption, hydric stress, and the water crisis. This water stress is based on freshwater availability and affects different levels (ecology, biology, economy, social, etc.) depending on the geographic location. Around 4 billion people live in areas that suffer from severe physical water scarcity for at least one month per year [3]; these regions are mostly located between the tropics and the Northern Hemisphere (Figure 1b, [4]). It is estimated that more than 1.8 billion people will live in regions without water, and two-thirds of the global population will live under hydric stress. Unfortunately, the scarcity of water and water quality deterioration go hand in hand with famine, low development of agriculture, and low social development.

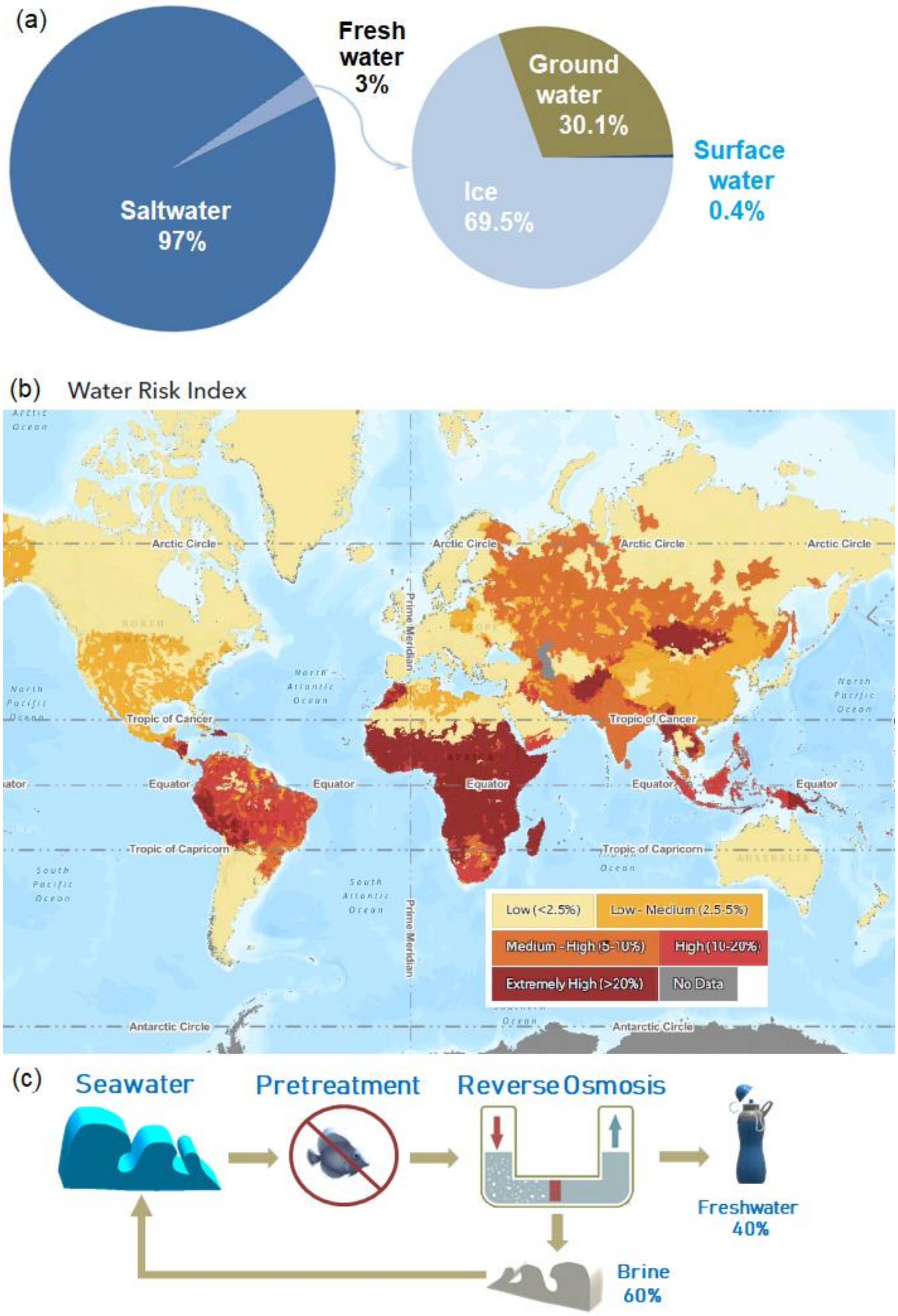

Figure 1. (**a**) Distribution of the total water on Earth in percentages (Source: [5]). (**b**) Water risk Index Map (Sources: [6,7]). (**c**) Desalination process.

According to the United Nations World Water Development Report [8], global water demand is expected to continue increasing at a similar rate until 2050, accounting for an increase of 20 to 30% above the current level of water use, mainly due to rising demand in the industrial, agricultural, and domestic sectors. Water demand is increasing, while supplies are shrinking (due to superficial and aquifer contamination, glacier melting, droughts, increasing urbanization, etc.). To cover this demand, the water industry must make better and more efficient use of available water resources, by means of water purification, water desalination, and waste water treatment and in industrial activities that require the use of water.

Due to the huge proportion of seawater (Figure 1a) and the fact that most countries have easy access to it (Figure 1b), one of the most feasible ways to obtain freshwater is through desalination. This water treatment is based on liquid–solid separation techniques such as evaporation and reverse osmosis (RO), but these techniques are not completely efficient (between 60–98%) due to the generation of a waste product known as brine (Figure 1c). A desalination plant operating using RO commonly recovers 40%, i.e., 0.40 m^3 of purified water is produced from each 1 m^3 of seawater, and 0.60 m^3 is transformed into brine to be discharged back into the ocean. The state of desalinization and brine discharges has been recently and thoroughly reviewed [9]. It is estimated that more than 15 thousand operational desalination plants produce 95 million m^3 of desalinated water per day, and more than 140 million m^3 of brine per day. Most of these plants are installed in the Middle East and North Africa (coinciding with areas under hydric stress, Figure 1b); although half of them are destined for industrial purposes, more than 62% of desalinated water is destined for human consumption. RO is by far the dominant treatment technology (84% of the operational plants).

The downsides of desalination are the intake and pretreatment strategies, use of land, elevated power costs, membrane separation saturations, chemical addition and biofouling, ecological and environmental problems associated with the brine returning into the sea, and social rejection [10–13].

The most abundant freshwater source is groundwater (Figure 1a), but continental brackish water occupies about 11% of aquifer volume and is located in the upland areas of sedimentary basins [14]. Desalination of geothermal and hypersaline water contained in aquifers is a possible alternative for municipal/agricultural supplies [14,15], but is also strongly linked to the extraction of minerals and elements with commercial value.

To achieve the objectives of sustainable development, there is a global challenge to obtain economically feasible high-quality water by means of "green technologies" to supply current and future hydric requirements. The main objective of this study is to show and discuss the results obtained using a new system (Adiabatic Sonic Evaporation and Crystallization, ASE&C) to separate water from solutes and solids associated with different saline and hypersaline samples (seawater and brines), obtaining a purified fluid (freshwater) and crystallized solids (with high potential commercial value). Also, this study analyses some performance tradeoffs to demonstrate the ASE&C system's feasibility in the treatment of seawater, brine, and other hypersaline fluids.

2. Materials and Methods

2.1. ASE&C Technology

A new innovative technology, termed Adiabatic Sonic Evaporation and Crystallization (ASE&C), was designed and patented (World International Patent Organization: EP3135635) for contaminated fluid purification using a physical approach, distillation for the separation of liquids and dissolved solids by promoting adiabatic changes and acceleration (Figure 2) [16]. In this case, it completely separated a seawater sample into freshwater and crystallized salts with a cost of energy between 0 and 20 kWh/m^3.

The specific energy consumption calculated by the ASE&C system is the total amount of power required for internal pumping and the heat exchanger. The required energy quantity for the ASE&C system depends on the complementary energy sources available.

The system consumes around 19.2 kWh/m^3 without any complementary energy source. If a residual heat source is available, the energy required to boost the water in the circuit is between 3–4 kWh/m^3. However, the energy consumption reaches 0 kWh/m^3 when the ASE&C technology is coupled to a hybrid solar thermal–photovoltaic system (for 24-h operation).

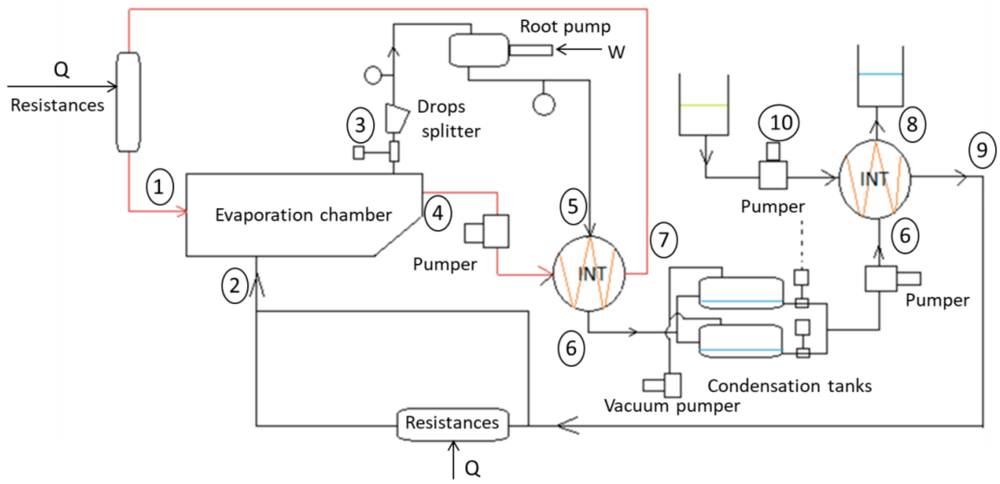

Figure 2. ASE&C™ flowchart diagram with energy feedback through vapor compression. 1. Inlet of the heat transfer fluid to the evaporator. 2. Inlet of the fluid to be processed (raw water) to the evaporator. 3. Output of the processed fluid (vapor) from the evaporator. 4. Heat-carrying fluid outlet from the root compressor. 5. Processed fluid (vapor) outlet from the root compressor to the heat exchanger. 6. Processed fluid (condensed) outlet from exchanger; after the fluid is condensed in the heat exchanger, it is deposited in two condensate tanks, and then taken to the condensate heat exchanger. 7. Exit of the heat transfer fluid after being heated by the exchanger. 8. Outlet of the processed fluid from the condensate heat exchanger. 9. Outlet of the fluid to be processed (raw water) from the condensate heat exchanger. 10. Input of the fluid to be processed to the condensate heat exchanger.

The ASE&C must be designed strategically to optimize the performance of the entire (zero-liquid discharge) ZLD system while depurating any contaminated fluid [17–20]. An improper design can reduce the overall efficiency or increase the operating costs.

2.2. Seawater Treatment

A volume of 79 L of seawater was supplied to the ASE&C technology; 77 L were ASE&C-treated and collected at the output of the systems (+1.3 L were used for the industrial set-up), and 0.7 L were collected for analytical purposes. For this particular case, the energy consumption was assumed to be 3–5 kWh/m^3.

2.3. Analytical Procedures

Aliquots from the liquid samples were collected in sterile bottles from the input and output for water quality analyses. Cations were determined by means of ICP-OES, anions by means of ionic chromatography/HPLC, carbonates and bicarbonates by means of Metrohm titration, and P with ICP-MS in certified laboratories as detailed in [17–20].

3. Results and Discussion

3.1. Seawater Treatment Results

Fluids collected before and after the ASE&C treatment were analyzed. Table 1 summarizes water parameters at the input and output of the ASE&C system. All the dissolved elements were almost completely removed (most of them below the analytical detection limit) to obtain distilled water with pH modified from 7.9 to 5.2, EC from 56 mS/cm to 142 µS/cm, and the Langelier index from 0.79 to −5.85.

Table 1. Physical-chemical analysis of water samples at the input (seawater) and the output (treated fluid).

Parameter		Input Sample (Seawater)	Output Sample (Distilled Water)
Langelier Index		0.79	−5.85
EC	µS/cm	53,327	142
pH		7.9	5.2
SS	mg/L	10	<3.0
COD	mg/L	1.1	0.6
Bicarbonates	mg/L	144.0	<5.0
Carbonates	mg/L	<0.2	<0.2
Nitrates	mg/L	<0.2	<0.2
Sulfates	mg/L	2524	<5.0
K	mg/L	403.7	<2.0
F	mg/L	1.4	<1.0
Br	mg/L	<0.1	<0.1
Ca	mg/L	421.2	<2.0
Mg	mg/L	1318.4	3.1
Na	mg/L	11,009.8	16.9
Cl	mg/L	18,200	30.9
B	mg/L	5.03	0.55

The values obtained for the crystallized salts formed are given in Table 2. Microbiological presence was not detected in the solid residue. Most of the newly formed conglomerates were chlorides (53%); 80.50% of the dried residue composition was NaCl, together with sulfates (4.80%), and Mg (3.34%).

Table 2. Crystallized solid salts' analysis after seawater treatment with the ASE&C system.

Microbiological Analysis		
Clostridium perfringens	absence/25 g	n.d.
Listeria monocytogenes	c.f.u./g	<20
Total coliforms	absence/g	n.d.
Intestinal enterococcus	absence/g	n.d.
Escherichia coli	absence/g	n.d.
Staphylococcus coagulase positives	absence/g	n.d
Mesophile aerobic microorganisms	c.f.u./g	<10
Mold and leaven (25 °C)	c.f.u./g	<10
Chemical analysis		
Fe	mg/kg	3.79
Ca	%	0.43
Humidity	%	<1
Insoluble residue	%	1.0
Sulfates	%	4.80
NaCl (over dried matter)	%	85
Mg (MgO)	%	5.54
B	mg/L	81.2
As	µg/kg	<25
Cd	µg/kg	<10
Zn	µg/kg	10,178
Co	µg/kg	<10
Cu	µg/kg	477
Mn	µg/kg	679
Hg	µg/kg	<5
Pb	µg/kg	132
K	mg/kg	8187

n.d.: not detected.

3.2. ASE&C Technology Coupled with RO

The ASE&C system can be coupled to the RO process to improve the efficiency of desalination. Applying the ASE&C depuration to brine (Figure 3) can improve the RO efficiency up to 100% freshwater recovery, so brine discharge into the ocean would be zero (ZLD), and a byproduct composed of crystallized commercial salts would be obtained (Figure 3a). Since brine from groundwater and inland reservoirs have different compositions, the pre-treatment and treatment are different, but the final products would be the same—complete freshwater recovery and dried crystallized salts with different compositions. The compositional chemistry of the Atlantic Ocean, the Mediterranean Sea, and brackish groundwater was studied in depth by [21]. This has an essential transcendence in the technoeconomic assessment of the efficiency process with the ASE&C system (material resistance and life cycle), the potential recovery process, and the revenue generated from the byproducts.

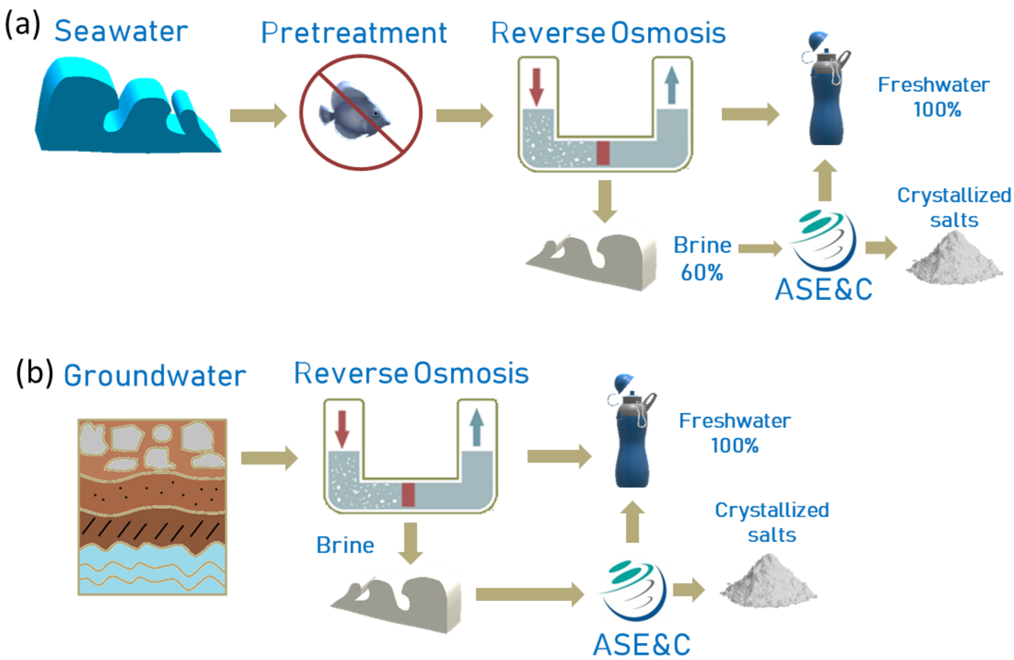

Figure 3. ASE&C coupled to the reserve osmosis cycle process for (**a**) the seawater desalination process and (**b**) groundwater brine treatment.

Some preliminary tests were adapted and run with different types of brine with different compositional and physicochemical characteristics (seawater and aquifer desalination) (Table 3). Three types of brine with different ranges of electrical conductivity were successfully separated into distilled water and crystallized solids (humidity < 1%). Brine A had an EC of 122 mS/cm and 78 g/L of TDS; it was oversaturated brine (hypersaline). Brine B was average seawater brine from desalinization (70 mS/cm and 44 g/L TDS). A third brine (Brine C), originally from brackish groundwater, had 28 mS/cm and 18 g/L TDS. Therefore, the ASE&C technology was adapted for the necessities of different types of fluids. The resulting products had similar volumes to the input, with chemical composition similar to distilled water (EC < 90 mS/cm, TDS < 60 mg/L) and removal of sulfates, chlorides and most of the dissolved elements (Table 3). The most interesting feature of the technology is the complete recovery of freshwater that can be used for other purposes with very low energy cost, but also the useful chemical compounds contained in the second byproduct as crystallized salts (with different compositions depending on the original fluid), with potential commercial value in the raw material market.

Table 3. Physicochemical characteristics of different brines (Brine A: hypersaline; Brine B: desalination brine; Brine C: groundwater brine) before (I) and after (O) treatment with ASE&C technology.

	Brine A		Brine B		Brine C	
	I	O	I	O	I	O
EC (mS/cm)	122,000	89	70,000	91	28,000	52
Eh (mV)	296	653	301	660	298	651
TDS (mg/L)	78,080	56	44,830	57	17,930	32
Sulfates (mg/L)	76,670	<5	4860	<5	3870	<5
Chlorides (mg/L)	67,060	<10	38,550	<10	14,569	<10
Na (mg/L)	35,990	<10	20,650	<10	6458	<10
Ca (mg/L)	1830	<10	1050	<10	986	<10
Mg (mg/L)	4880	<10	2810	<10	1860	<10
K (mg/L)	1463	<5	843	<5	453	<5
Bicarbonates (mg/L)	611	<5	351	<5	654	<5
Br (mg/L)	416	<0.1	240	<0.1	44.8	<0.1
Ga (mg/L)	650	<0.01	589	<0.01		<0.01
Sr (mg/L)	52	<0.01	29	<0.01	14.4	<0.01
Li (mg/L)	2.7	<0.01	1.6	<0.01		<0.01
B (mg/L)	17	<0.05	9.8	<0.05		<0.05
Rb (mg/L)	0.52	<0.01	0.28	<0.01		<0.01

Recovering metals, metalloids and rare earth elements as a byproduct of depuration activities is challenging, but some important concentrations are found in brines, such as lithium, rubidium, and potassium. Thus, extraction from brines and other waste streams is becoming economically viable, as previously reported in [16] with mining lixiviates depurated with the ASE&C technology.

Desalination processes require physical and chemical pre-treatment (reduction of algae and corrosive material, etc.) [22] (Figure 1c), but the cleaning processes of membranes increase the chemical components in the disposal brine. However, lately, the challenge in water desalination has involved two byproducts: freshwater and solid salts [23]. Therefore, in the race to obtain better water quality, brine may be an excellent potential source. Brine mining is commonly used to extract numerous materials from the same deposit (e.g., lithium carbonate, magnesium chloride, potassium chloride), regardless of brine origin. New technologies for the separation and recovery of sources from seawater and brine are appearing [23]. Sodium chloride from salt extraction is the most ancient resource exploited from seawater, but some others, such as Au, Mg and Br, have also been extracted throughout history [24]. The new trends in mineral market prices and critical raw materials highlight the interest in the search for new sources such as brines [21,25]. Na, Ca and Mg are elements that can be found in greater concentrations in oceans and brackish groundwater [21]. Some elements, although low in concentration, play an important role in the world market due to their technological applications; among them are Li, Rb and Sr, as well as trace elements such as rare earth elements.

Ref. [21] analyzed the economic potential of brine mining from desalination rejects containing B, Ca, Sr, Mg, Na, Li, Rb and Ga; they concluded that the economic value might range from EUR 13 billion to 29 billion annually. However, annual estimations (gross profit) for the complete recovery of elements with the studied brines (Table 3), applying the same prices to a production capacity of 1000 m^3/day, ranged from EUR 1 to 11 million for Brine A and Brine B, and from EUR 10 to 21 thousand for Brine C (Table 4). More than 96% of the revenues of Brine A and B come from gallium, due to its elevated market price. Gallium also has specialized uses in small quantities, e.g., optoelectronic devices, with economically viable recovery from seawater and other highly concentrated sources [26]. There would also be an important recovery of rubidium from Brine B. This rare alkali metal has high economic value for its emerging industrial applications (biomedicine, solar cells, electronics, etc.); it is extracted from land-based mineral ore sources (as a fraction of ores) [27]. However, [27] other alternative sustainable sources such as seawater brine or salt lake brines, with less energy extraction consumption and greater concentration than land ores, have been suggested. Some hydrometallurgical techniques can effectively separate Rb as rubidium carbonate (98%) from brines [28] and other minerals and brines [29].

Table 4. Potential economic range value (minimum–maximum in thousands of EUR) of the elements recovered from the waste of brines calculated for an annual depuration capacity of 1000 m^3/d and considering analytical data and market prices from [21].

	Seawater	Brine A	Brine B	Brine C
Na	2692–8117	24.11–72.7	13.8–41.7	4.33–13.0
Ca	66–291	0.79–3.46	0.5–2.0	0.43–1.9
Mg	148	15.03	8.7	5.7
Ga		1104–11,340	1000–10,275	
Sr		0.52–2.94	0.29–1.64	0.14–0.82
Li	703–755	1.03–1.11	0.61–0.66	
B	22–28	0.013–0.02	7–9	
Rb		4.91–6.31	2642–3396	
Total (thousands of EUR)	3631–9338	1150–11,441	1026–10,333	10.62–21.45

Almost all the revenue from Brine C comes from a combination of Na and Ca due to their high concentrations (there are missing data for the other elements). Calcium removal from seawater/brine has dual benefits: it improves the RO (secondary scaling) [25] and market potential (0.43–1.89 EUR/kg, [21]), thereby minimizing desalination costs. Calcium is sold as calcium carbonate pellets when produced from brackish water, and calcium sulfate when produced from seawater [25]. Sodium, as different sodium compounds (sodium chloride, sodium sulfate), is sold for many purposes (the food industry, cosmetics, and ice-melters, among others). Despite its low market price in comparison to other elements (0.67–2.02 EUR/kg, [21]), its elevated concentrations in seawater and brine make this element economically interesting.

The approximation was also calculated for seawater with the available data. The annual benefits obtained ranged (for Na, Ca, Mg, Li and B recovery) from EUR 3 million to 9 million, based on 75–87% Na recovery and 8–20% Li recovery. The strong uncertainty regarding the availability of Li and the pegmatite ores has raised interest in brine/seawater as a new potential source [25]. Although Li concentration in these materials seems very low (average 1.24 g/m^3, [21]), it can increase significantly after treatment with RO or other methodologies such as ASE&C, reaching economically feasible extraction from brines and solids (in the case of the ASE&C). Li extraction from brines, such as electrochemical extraction, is more developed from the point of view of environmental friendliness and competitiveness [30].

3.3. ASE&C Technology Competitive Advantages

(i) The ASE&C system is a cost-effective water quality treatment which does not need sample pre-treatment (it does not use chemical reagents). The resultant fluid from the treated seawater achieves 100% removal of most of the elements (Tables 1 and 5).

(ii) It is an energetically versatile low-cost technology (0–20 kWh/ m^3) when coupled to solar thermal energy, photovoltaic, residual heat, biomass, etc., considering that it requires electricity or heat for the operation.

(iii) The final two potential commercial byproducts (clean freshwater and commercial crystallized salts) could offset operational costs as a promising secondary source. It has been demonstrated that 100% distilled water can be produced from contaminated effluents. Volumes of 100 m^3 per day were treated and tested under controlled conditions for several weeks, demonstrating the production of 100 m^3/d distilled water (pilot plant). This is also scalable up to the treatment of 600 m^3/d to recover the same amount of water (a 40-foot plant); however, it is scalable to higher volumes, as replicates of this approach will not have limits in their design. Regarding the production of dry conglomerates, it obtains 95–99% of the total solutes included in the original input fluid.

(iv) The CO_2 footprint of the ASEC&C technology is estimated at 0.2 tons (for production of 600 m^3/d and 5 kWh/m^3), so these emissions would be approximately null if using photovoltaic and thermo-solar panels as a source of energy. Thus, considering a consumption of 5 kWh of electric energy, it would emit 0.5 kg/CO_2 eq m^3.

(v) This technology can be adapted to other fluid characteristics for a properly efficient process, and indeed has already been tested on some of them [16]. ASE&C is a portable module occupying 40 feet of container space and may be placed anywhere, but could also be designed as a full plant for higher volumes of fluid treatments.

(vi) It complies with the legislation of the EU Water Framework Directive [31–33] and the UN Sustainable Development Goals (SDGs) to achieve good ecological status of water bodies. The ASE&C effluent produces distilled water that can be reused for different purposes, such as industrial processes and human consumption; it might be injected in wells to fill and purify aquifers; after remineralization, it is suitable for drinking; it is suitable for irrigation after mixture with aquifer water; and it could also be dumped in superficial water, achieving good ecological status.

Table 5. ASE&C vs. other competing technologies (reverse osmosis: RO, evaporation and crystallization).

Feature	RO	Evaporation	Crystallization	Evap + Cryst 2 Steps	ASEC
Water/solid separation	45%	80%	80–100%	90–100%	100%
Energy consumption (kWh/m^3)	3–5	80	250–500	130–230	0–20 *
Use of chemicals	Yes	Yes	Yes	Yes	No
CAPEX (€/m^3)	700–2000	15,000	20,000–40,000	30,000	5000–15,000
Environmental concerns	Brine discharges	Brine discharges	High CO_2 emissions	Brine discharges	ZLD Low CO_2-missions

* variation depending on energy sources available, see Section 2.1.

One study [13] recognized several impact mitigation strategies, associated with (i) source water intake, (ii) brine discharge (water recovery, energy recovery, extraction of precious materials, beneficial use of brine), (iii) energy use, (iv) site selection, and (v) impact on the environment. The ASE&C can completely solve three of them and the others to a partial extent.

Other technologies for freshwater recovery of mineral extraction from brines are less efficient, imply high energy consumption, and require the addition of products and chemicals (Table 5). Although some of them have lower CAPEX values, they also include several environmental concerns (especially brine discharges). RO and ion exchange units are commonly used in lithium recovery from geothermal brines [34]. Direct lithium extraction employs significant volumes of water and chemicals, has high energy consumption, and generates wastes [35]. In contrast, other evaporitic technologies employed in brine mining (such as lithium extraction) have intensive water use, protracted duration, and particular use over continental brines [35]. Ultrafiltration combined with RO and/or nanofiltration have recently been used [36]. Some other zero-discharge desalinations use hybrid desalination with RO and nanofiltration or electrodialysis, metathesis and evaporation ponds, with significant recovery of water (97%) and fractions of multivalent ions (60%), but also with substantial energy consumption (0.77 kWh per g TDS/L^{-1}) [37] and potentially detrimental effects due to the costly use of membranes and chemicals.

4. Conclusions

The ASE&C technology can treat brackish water and seawater, including their brine waste from RO desalination, with complete separation of water as distilled water and crystallized salts (humidity < 1%), using very little energy (0–20 kWh/m^3). This study presents the results of the efficiency of separation in terms of physicochemical analysis. Laboratory results showed that the two byproducts derived (freshwater and crystallized salts) have commercial potential, and point to a paradigm shift in desalination processes, because of the zero-brine discharge converted to commercial salts, the implementation of the circular economy, and the avoidance of environmental concerns related to brine discharge back into the ocean.

The preliminary results demonstrated that the technology can be adapted successfully to different types of fluids with a wide range of electrical conductivity. Thus, the ASE&C technology coupled with the existing RO treatment plants might help to solve environmental problems associated with brine discharges, but it also supposes an alternative method of producing raw materials for brine mining. Annual economic estimations based on the studied samples were calculated: they averaged EUR 6.5 million when ASE&C is coupled with a seawater RO desalination plant (Na recovery was the greatest contributor, followed by Li). Other brine recoveries provided greater variable benefits (average benefits of EUR 4 million, and maximum benefits of EUR 11 million) due to composition disparity, with important recovery of Ga, Mg, and Na.

The innovative ASE&C technology transforms brines and improves water solutions to help reduce costs and waste volume, while increasing byproduct values with a low carbon footprint.

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