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SWRO Brine Characterisation and Critical Analysis of Its Industrial Valorisation: A Case Study in the Canary Islands (Spain)

Ángel Rivero-Falcón [1,*], Baltasar Peñate Suárez [1] and Noemi Melián-Martel [2]

[1] Water Department, Canary Islands Institute of Technology (ITC), 35119 Santa Lucía, Spain; baltasarp@itccanarias.org
[2] Department of Process Engineering, Industrial and Civil Engineering School, Universidad de Las Palmas de Gran Canaria, 35017 Las Palmas de Gran Canaria, Spain; noemi.melian@ulpgc.es
* Correspondence: ariverof@itccanarias.org

Abstract: The most recent years of research have shifted the perception of desalination brine from being waste to a high-value resource, in consonance with a circular economy perspective. The Canary Islands, containing the largest number of desalination plants per square kilometre in the world, are a perfect location to study its characteristics and evaluate its potential. A total of 10 heterogeneous seawater reverse osmosis plants were selected to determine the brine's physicochemical characterisation, comprising 37 parameters, and its correlation to the technical and operational aspects of the desalination plants. The results show a stable narrow range of the percentage of major ions concentration in relation to the total dissolved solids (55% Cl^-, 29.5% Na^+, 8% SO_4^{2-}, 4% Mg^{2+}, 1.5% Ca^{2+}, 1.2% K^+, 0.5% HCO_3^-, and 0.2% Br^-) irrespective of specific differences between plants. The results obtained in this study are highly beneficial to industrial suppliers and future users of desalination brine valorisation (DBV) technologies, allowing an estimation of the chemical composition of a brine through knowledge only of its conductivity. Such information is crucial before investing in and optimizing DBV technologies. Nonetheless, from an environmental, economic, operational, energy-based, and R&D point of view, several improvements are required to promote their large-scale feasibility and viability.

Keywords: desalination; brine; seawater reverse osmosis; brine characterisation; industrial valorisation; brine mining

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Citation: Rivero-Falcón, Á.; Peñate Suárez, B.; Melián-Martel, N. SWRO Brine Characterisation and Critical Analysis of Its Industrial Valorisation: A Case Study in the Canary Islands (Spain). *Water* **2023**, *15*, 1600. https://doi.org/10.3390/w15081600

Academic Editors: Monzur Imteaz and Amimul Ahsan

Received: 3 March 2023
Revised: 12 April 2023
Accepted: 18 April 2023
Published: 20 April 2023

1. Introduction

One of the biggest challenges that humankind faces today is assuring the supply of the growing demand for fresh water all over the world. A constant increase in the population along with the over-exploitation and contamination of the conventional water sources created the obligation decades ago of finding alternative ways to provide clean and safe water to the population. Since then, seawater desalination has become an essential necessity in many parts of the world. The total desalination operating capacity in 2021 was 79.35 million m^3/day, produced by approximately 18,000 desalination plants worldwide [1]. Approximately 85% of these plants operate with reverse osmosis (RO) technology, and this percentage is likely to rise as RO technology also represents nearly 91% of the desalination plants presently under construction [2], including the largest plants in the world, designed to produce up to 1 million m^3 of fresh water daily.

Despite being an optimised technology, close to reaching its thermodynamic limit [3], the technical and scientific communities continue in their efforts to perfect the process from different points of interest: energy, environment, and economy. There are two main challenges at the top of the list: reducing the energy dependence and CO_2 emissions associated with the energy required by desalination plants, and converting the main waste of this process (brine) into a valuable resource [4]. Numerous studies have been published on the environmental impacts for flora and fauna caused by the discharge of desalination brine (DB) into coastal waters [5–7], as well as on the specific technologies to minimise those adverse environmental impacts such as the use of venturi diffusers [8]. Spain, especially in the Canary Islands and along the Mediterranean coast, has always been at the forefront of the analysis of the environmental impacts of brine, as well as its potential. Converting DB from waste to a resource following circular business strategies is a unanimously accepted need.

The Canary Islands (Spain) are an archipelago located in the eastern North Atlantic Ocean off the coast of northwest Africa. The Canary Islands, with a coastal seawater salinity range of 36.7–36.9 g/L [9], have a long history in the desalination industry [10], starting with the construction of the first desalination plant in Europe in 1964, in Lanzarote. Since then, the number of seawater desalination plants in the archipelago has grown to an estimated total of 205 [11], accounting for around 1% of the installed desalination capacity worldwide. In 2020, the registered volume of DB in the archipelago was nearly 429,000 m^3/d [12]. During this past decade, politicians, the industry sectors, and social actors have all introduced the notion of a circular economy as a vital concept [13]. In March 2020, the European Commission adopted the new Circular Economy Action Plan [14] as one the pillars of the European Green Deal. In Spain, the Spanish strategy for the circular economy is called "España Circular 2030" [15]. The Canary Islands have also developed their own legislation regarding the circular economy with the creation of the 2021–2030 Canary Islands Circular Economy Law [16]. Water reuse, including the brine from desalination plants, figures heavily in this legislation in connection with the also recently approved regional strategy for a blue economy. In general, the desalination industry explores the circular economy from three different perspectives: increasing the life span of RO membranes or reusing and recycling them [17,18], eliminating hazardous chemical products [19,20], and brine management and treatment [4].

There is also a growing interest in the concept of desalination brine valorisation (DBV), with resource recovery, electric power generation, and carbon capture and utilisation (CCU) as the main alternatives that are being explored [21]. Figure 1 shows the exponential increase in the number of articles worldwide related to DBV, from zero publications in 2000 to more than 29 in 2022, with 103 studied published in the past 5 years (Figure 1). Enormous efforts have been made in the search for a solution to this challenge which is technically and economically feasible and, at the same time, sustainable and respectful of the environment. However, to date very few pilot-scale research studies have been undertaken [4].

Notwithstanding their potential (brine valorisation and resource recovery), neither developments through innovative and disruptive processes nor adaptations and improvements to already established technologies have yet achieved a level of maturity which could imply a radical transformation in the desalination industry in the short term.

The physical and chemical characterisation of DB is crucial before evaluating any DBV technology. Bello et al. [22] summarised the chemical characteristics of brine from various desalination plants in different countries. The brine from seawater reverse osmosis (SWRO) desalination plants displays similar properties in different parts of the world. However, the research data to date have tended to focus on one specific DB chemical analysis, providing absolute values of certain parameters regardless of the different variables affecting those values, such as plant location or operating conditions (recovery rate, pre-treatment, type of intake, etc.), rather than evaluating the differences these factors could make to specific desalination brines.

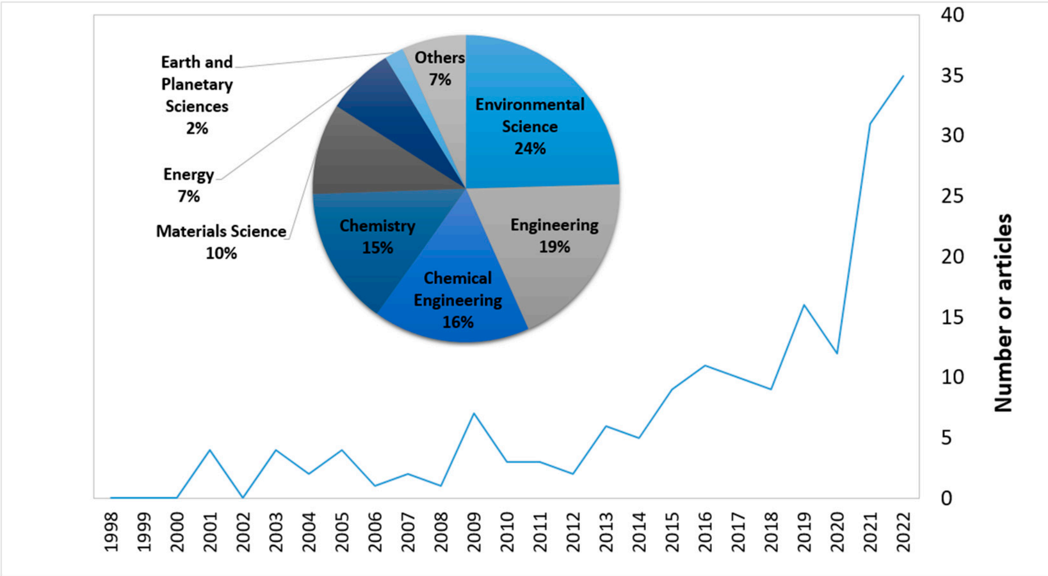

Figure 1. Evolution over the past 25 years of the number of journal articles with topic keywords "brine mining" OR "brine management" OR "brine treatment" OR "brine valorisation" OR "resource recovery" AND desalination in article title, abstract, or keywords.

A good knowledge of the exact chemical composition of a DB would allow the DBV technology providers to assess valuable information about the suitability of their process, the pre-treatment requirements, and the maximum quantity of chemical by-products obtainable, aspects which directly affect the economic viability of any proposal. Furthermore, the presence of a specific compound might be detrimental to a particular DBV process and its concentration value could induce DBV technology owners to optimally select from among several desalination plants.

In order to develop a successful DBV application, the primary aim of this paper is to increase the knowledge about the physicochemical characteristics of DB by generating a complete profile/categorisation of SWRO brine in the Canary Islands from desalination plants within the framework of the DESAL+ Living Lab platform [23], including the chemical and physical characteristics. An additional aim is to guide technology providers and end users through the presentation of the latest technological developments and an analysis of the industrial valorisation of DBV processes and technologies including the potential strengths, barriers, and limitations.

1.1. Desalination Brine Valorisation Technologies

The majority of DBV technologies, which are targeted at either increasing the recovery of desalinated water, generating chemical by-products, or producing electric power, can be classified according to the three DBV stages of pre-treatment, concentration, and conversion [23].

Figure 2 shows in a simplified way these three stages. The desalination brine would first pass through a pre-treatment stage, where the main objective is usually to separate the detrimental elements from the brine, mainly divalent ions such as calcium (Ca^{2+}), magnesium (Mg^{2+}), and sulphates ($SO_4{}^{2-}$) [24]. Removing these ions in advance helps to reduce inorganic scaling problems, and in this way contributes to optimising the following stages. Multiple minerals and metals can be extracted from the brine. This stage can also generate chemical by-products derived from these ions (e.g., calcium carbonate ($CaCO_3$), magnesium hydroxide ($Mg(OH)_2$) [25], and calcium sulphate ($CaSO_4$) [26]) by chemical precipitation, potentially enhancing the economic viability of the overall process on the assumption that the by-products obtained could be commercialised. Nanofiltration technology is one of the most interesting pre-treatment choices, separating the brine into two different solutions: a monovalent-rich and a divalent-rich solution, with a much lower operating pressure than is required in RO processes. The two new streams can then become the feed for different DBV technologies, increasing their performance [27].

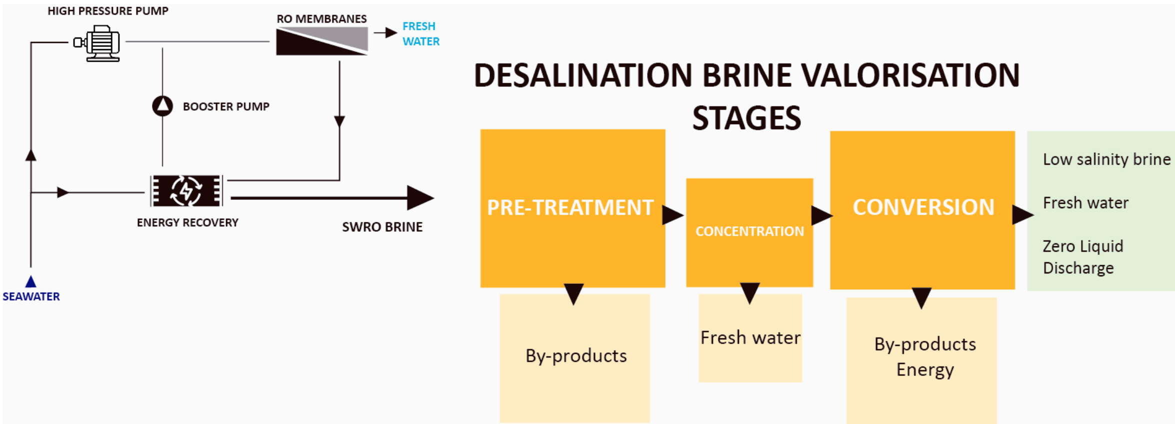

Figure 2. Brine valorisation generic flow diagram showing its three different stages.

Following this stage, the pre-treated brine would go through a concentration stage, where the appropriate technology obtains more fresh water from the brine, hence concentrating it. This stage depends directly on the requirements of the subsequent conversion technology. Lately, brine concentrators using membranes have been replacing thermal concentrators [28]. Many conversion technologies benefit from a more concentrated brine, especially those which have as a goal the generation of chemical by-products, while other technologies even need a minimum concentration to be able to operate (e.g., in the electrolysis process for the chlor-alkali industry, the minimum required brine concentration is 260 g/L [29]).

The final stage of any brine valorisation process is the conversion stage, where the pre-treated and perhaps concentrated brine is transformed into either other liquid components or solid salts and minerals. At this stage, the chemical composition of the brine is mainly sodium chloride (NaCl). Acids and bases, such as hydrochloric acid and sodium hydroxide, can be produced from brine by electrochemical technologies such as bipolar membrane electrodialysis (BMED) [30]. Similarly, another valuable product, sodium hypochlorite (NaClO), can also be obtained through an electrochemical process [31]. Apart from liquids, inorganic salts can also be obtained in this conversion stage (e.g., NaCl and $NaHCO_3$) [32], as well as dilution of the remaining brine and, hence, the minimisation of the environmental impacts of the discharge into the sea of a more concentrated brine.

Another approach to DBV is to take advantage of the osmotic pressure gradient that exists between DB and a low salinity solution. Forward osmosis (FO) is an emerging technology which operates with a semipermeable membrane that separates the two solutions and, by means of natural osmosis and with minimum pressure required, allows water molecules to move from the low concentration solution to the brine; therefore, in this case, diluting it. Electrical energy can also be generated by combining brine with low conductivity water (e.g., secondary effluent from a wastewater treatment plant) [33], as a result of their osmotic pressure gradient, through the application of technologies such as pressure retarded osmosis (PRO) [34,35] or reverse electrodialysis (RED) [36]. In all these processes, the low salinity solution will become more concentrated and the SWRO brine more diluted. The brine can then be discharged into the sea with minimal environmental impact due to its similar salinity with the seawater or can be redirected to the inlet of an RO system for the production of fresh water for agriculture, for instance. Consequently, planning the construction of large desalination plants close to wastewater treatment plants in order to be able to reduce the associated energy consumption could be a worthwhile model in the future.

The consideration of brine as a resource instead of as waste [37] can also be seen in the use of brine to capture CO_2 [38], helping to reduce climate change inducing CO_2 emissions as well as producing valuable by-products which include, among others, sodium bicarbonate ($NaHCO_3$).

In many cases, specific advances are required in the performance of selective membranes or in the optimisation of the processes employed in emerging technologies such as membrane distillation (MD) [39,40], high pressure reverse osmosis (HPRO) [41], or selectrodialysis with bipolar membranes (BMSED) [42], to mention a few.

The aforementioned technologies and processes do not completely avoid brine discharge. The concept of zero liquid discharge (ZLD) [43], which essentially comprises the intention to fully exploit the brine, involves a combination of different processes targeted at the eradication of any liquid discharge, the maximisation of water production and the generation of as many by-products as possible. In the past, thermal processes [44], including multistage flash distillation (MSF), multi-effect distillation (MED), spray drying (SD), and vapour compression evaporation (VCE) have been implemented to produce different salts depending on their solubility. Until recently, thermal processes had been practically the only available choice. However, in order to optimise those operations, lately there has been a shift from thermal processes to membrane technologies [45], including membrane crystallisation (MCr), a variation of the membrane distillation (MD) process, by which the brine reaches the supersaturation point, forming crystals. Some companies are starting to offer new solutions adapted to specific types of feed water in terms of salinity, temperature, pre-treatment, and even taking into account the local demand of the extracted products. The economic feasibility of a specific process will vary depending on such characteristics. With another concept, minimal liquid discharge (MLD) [46], the last and most energy demanding stage of a ZLD process is avoided, generating a final brine that is highly concentrated but at a considerably lower processing cost.

Whether the selective extraction of targeted compounds or an MLD/ZLD route is applied, energy consumption tends to be the main variable that needs to be tackled for the development of a feasible process. It therefore seems logical to consider renewable energies as the perfect partner to minimise the carbon footprint of brine treatment processes.

While Figure 2 is a simplified generic diagram of DBV processes, multiple variations can be found depending on the different technologies used and the desired output. Table 1 shows the most significant DBV technologies and their allocation within the three previously described stages. Complete descriptions of the different technologies can be found in several reviews in the literature [44–46].

Table 1. Classification of the main desalination brine valorisation (DBV) technologies by stages, adapted from [44–46].

Pre-Treatment	Concentration	Conversion
Chemical precipitation (CP)	Forward Osmosis (FO)	Bipolar Membrane Electrodialysis (BMED)
Nanofiltration (NF)	Osmotically Assisted Reverse Osmosis (OARO)	Membrane Crystallisation (MCr)
Carbon Capture and Utilisation (CCU)	Membrane Distillation (MD)	Pressure Retarded Osmosis (PRO)
Selective Electrodialysis (SED)	Electrodialysis Metathesis (EDM)	Reverse Electrodialysis (RED)
Ion Exchange resins (IEx resins)	Temperature Swing Solvent Extraction (TSSE)	Electrolysis (chlor-alkali)

2. Materials and Methods

With the aim of increasing the knowledge of the characterisation of brine and the determination of indicative DBV factors and of providing an insight into its industrial valorisation, the methodology of this research is divided into two sections: a brine physico-chemical analysis and a determination of the different factors used to analyse the potential strengths and barriers/limitations of industrial scale DBV processes.

2.1. Brine Characterisation Analysis

In absolute terms, certain elements can be found in higher volumes in seawater than in mineral reserves on land. One such example is magnesium [47], classified as one of the critical raw materials by the European Commission in 2020 [48] as a result of both its importance for the economy of Europe and the dependence on its importation. Lithium is another clear example [49], the demand for which has increased radically in recent years because of its use in Li-ion batteries. In addition, elements perhaps less expected, such as uranium [50], caesium, or rubidium [51], could also be extracted from brine through adsorption, extraction, and ion exchange processes.

Several factors have a direct influence on the chemical composition of any SWRO brine. These include plant location, type of intake (open sea water or beach well), and the operating conditions, with the latter associated to the physical and chemical pre-treatment processes (including the addition of antiscalants), number of RO stages, fresh water capacity, water recovery of the RO system, and even the ageing of the system and membranes.

In order to understand the differences in terms of the brine chemical composition in the Canary Islands, a study comprising 10 SWRO desalination plants was carried out. The heterogeneous selection of the plants was made considering the following characteristics: fresh water daily production (pilot plant, low scale, medium scale, and high scale), type of intake (open sea water or beach well), physical and chemical pre-treatment, number of stages, and recovery rate, as can be seen in Table 2. These desalination plants are all integrated in the research ecosystem created within the framework of the DESAL+ LIVING LAB platform [23] in this archipelago.

Table 2. Characteristics of the seawater reverse osmosis (SWRO) desalination plants selected.

SWRO Desalination Plant	Intake	Physical Pre-Treatment	Chemical Pre-Treatment	Fresh Water Production (m^3/d)	Average Feed Conductivity @ 25 °C (µS/cm)	Number of Stages	Average Recovery Rate (%)	Average Brine Conductivity @ 25 °C (µS/cm)
DP#1	Beach well	Sand and cartridge filters	No	15,000	52,000	1	45.0	84,500
DP#2	Beach well	Sand and cartridge filters	Antiscalant	100	55,500	1	36.5	80,000
DP#3	Open sea water	Sand and cartridge filters	$NaHSO_3$	5000	55,000	1	41.0	82,500
DP#4	Open sea water	Sand and cartridge filters	Antiscalant	79,000	55,000	2	50.0	96,000
DP#5	Beach well	Only cartridge filter	No	3000	53,500	1	40.0	82,500
DP#6	Open sea water	Ultrafiltration and cartridge filter	HCl + NaClO + Antiscalant	14,750	55,500	1	45.5	89,000
DP#7	Beach well	Sand and cartridge filters	NaClO + $Na_2S_2O_5$ + Antiscalant	1800	55,000	1	42.0	84,500
DP#8	Beach well	Sand and cartridge filters	No	5200	52,500	1	42.5	84,000
DP#9	Beach well	Only cartridge filter	Antiscalant	33,000	54,000	2	54.0	97,500
DP#10	Beach well	Sand and cartridge filters	Antiscalant	16,500	48,500	1	45.0	81,000

Essential data from each desalination plant was collected through various visits to the plants, including general information, technical characteristics of the plant (water intake, pre-treatment, and number of RO stages), operating conditions (fresh water daily production, and water recovery), and feed water and brine data (temperature, conductivity, and pH) measured with a sensION™+ MM150 from Hach Lange, calibrated specifically for high conductivity solutions.

The selection of desalination plants shows heterogeneity in terms of fresh water production, including a pilot plant of 100 m^3/d as well as small-scale (<10,000 m^3/d), medium-scale (10,000–20,000 m^3/d), and large-scale plants (<20,000 m^3/d), with fresh water production rising to as much as almost 80,000 m^3/d.

Different brine samples were collected for chemical analysis. Care was taken to ensure the samples were representative of a standard brine generated under normal conditions, without any technical issues, cleaning, or maintenance operations in the desalination plants during or immediately before the sample collection. The temperature, pH, and conductivity values were measured in situ, in addition to actual water flows (feed, permeate, and brine) and water recovery. Three different samples from two different years (2021 and 2022) were collected and analysed to ensure repeatability. Additionally, a comprehensive chemical composition was carried out through an analysis of a total of 37 parameters (electrical conductivity at 20 °C, pH, and F- by electrometers; total dissolved solids (TDS) by gravimetry; total organic carbon (TOC) by FTIR; total N by chemiluminescence; total P, Al, As, Ba, Cd, Co, Cu, Cr, Sn, Fe, Li, Mn, Ni, Pb, V, and Zn by ICP-MS; SiO_2, Ca^{2+}, Mg^{2+}, K^+, Na^+, B, Sr, and Mo by ICP-OES; Br^-, Cl^-, and $SO_4{}^{2-}$ by HPLC; HCO^{3-} by titration; NO^{3-} by cadmium reduction; $PO_4{}^{3-}$ by absorption spectroscopy; and Hg by atomic fluorescence spectroscopy) for each brine sample, following international standards, in an external laboratory accredited by UNE-EN ISO/IEC 17025:2017. This list of parameters contains the major ions present in SWRO brine, some metals and minerals studied by the Sea4Value project [52], and other parameters referred to water quality standards [53,54].

2.2. Identification of Industrial DBV Factors

The technologies and processes aimed at generating value from desalination brine have not yet reached an industrial scale. Many are still considered emerging technologies while others have not even evolved from laboratory tests. Instead of comparing different emerging technologies for brine desalination [55], the idea in the present study is to elaborate an overall analysis of the implications of industrial scale DBV processes, defining a list of factors to assess their possible strengths and barriers/limitations.

With the aim of showing a roadmap for both DBV technology providers and potential users, different perspectives have been considered: environmental, economic, operational, energy-based, R&D, commercial, and social. The successful industrialisation of DBV solutions lies in taking advantage of the strengths and being aware of and, when possible, overcoming the barriers and limitations found.

Although a single solution that fits all scenarios seems improbable, Table 3 shows a list of factors that need to be taken into account in order to develop successful industrial DBV solutions. These will be classified and explained in more detail in Sections 3.2 and 3.3.

An initial evaluation, resembling a quantitative risk assessment matrix, will be used to highlight the most critical barriers/limitations for the industrialisation of DBV processes. According to the information shown in Section 3.3, both the likelihood and impact of the nine barriers/limitations identified in Table 3 will be evaluated quantitatively and given, in each case, a score between 1 and 5. The product of the two aspects will show the overall relevance of each factor.

Table 3. Classification of factors for DBV industrialisation.

		Environmental	Economic	Operational	Energy-Based	R&D	Commercial	Social
Strengths	Environmental impact mitigation of brine discharge	X						X
	Resource/energy recovery		X		X			
	Desalinated water production increase		X					
	Hybrid solutions/ZLD			X	X			
	Integration with renewable energies and waste heat	X			X			
	New employment opportunities							X
Barriers/limitations	Pre-treatment		X	X				
	TRL of emerging technologies					X		
	Environmental impact	X						
	High Capex/Opex		X					
	Legal restrictions			X				
	Limited available research data					X		
	Commercialisation of by-products			X			X	
	Lack of specific materials/components					X	X	
	Lack of specific simulation software					X		

3. Results and Discussion

3.1. Brine Characterisation and Categorisation of SWRO Brine in the Canary Islands

The different ranges of the recorded feed (light blue) and brine (dark blue) conductivity values are shown in Figure 3. Seawater conductivity values (feed) do not differ much among the different desalination plants, apart from DP#10 whose feed contains a mix of seawater and brackish water, and hence has a lower conductivity value. The variation among brine conductivities is directly influenced by the number of stages of each desalination plant (DP#4 and DP#9 are two-stage RO plants while the others are single-stage RO plants) and their specific water recovery rates. This study comprises SWRO brines with a large variation in terms of conductivity values, from as low as 75,000 µS/cm to as high as 100,000 µS/cm (conductivity values @ 25 °C).

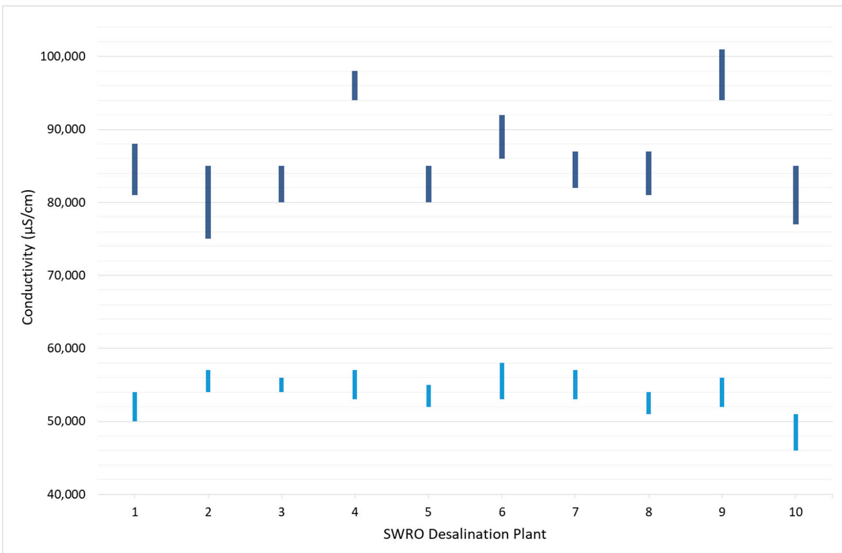

Figure 3. Feed (light blue) and brine (dark blue) conductivities (@25 °C) of the desalination plants included in this study.

The average results of the chemical composition analysis of the brine samples are represented in Table 4. The values for each of the 37 parameters analysed are shown, including the major ions present in the SWRO brine.

Table 4. Chemical composition of the brines from 10 desalination plants in the Canary Islands.

Parameter	Unit	DP#1	DP#2	DP#3	DP#4	DP#5	DP#6	DP#7	DP#8	DP#9	DP#10
EC@20 °C	µS/cm	76,750	71,000	75,450	86,867	74,300	83,050	76,100	76,800	89,350	72,550
pH	U. pH	7.6	7.4	8.0	7.9	7.5	8.0	7.9	7.0	7.6	7.4
TDS	mg/L	63,375	58,756	62,972	70,444	62,080	66,120	63,595	63,743	71,356	59,333
Cl^-	mg/L	34,730	32,510	35,000	39,120	33,890	36,420	34,875	34,645	39,645	32,975
Na^+	mg/L	19,207	17,761	18,330	20,507	18,740	19,987	18,975	19,217	21,070	16,869
SO_4^{2-}	mg/L	5230	4630	5030	5423	4900	5150	5116	4970	5593	4765
Mg^{2+}	mg/L	2297	2105	2648	3036	2451	2480	2646	2396	2760	2453
Ca^{2+}	mg/L	704	703	800	969	798	801	736	1181	957	1085
K^+	mg/L	742	620	777	916	732	789	828	617	825	588
HCO_3^-	mg/L	287	203	235	296	388	276	252	398	261	324
Br^-	mg/L	122	146	125	142	120	186	139	147	152	169
Sr^{2+}	mg/L	19.9	20.3	18.8	22.1	18.7	21.9	19.4	38.3	27.1	31.7
SiO_2	mg/L	15.4	48.2	<2.4	<2.4	29.7	<2.4	<2.4	78.9	49.1	43.1
B	mg/L	7.1	6.3	7.2	8.4	8.1	8.0	7.6	6.5	8.6	6.1
TOC	mg/L	1.0	0.7	1.4	1.8	0.7	1.4	1.1	1.1	0.9	1.0
NO^{3-}	mg/L	13.5	2.9	0.2	3.3	4.0	0.4	1.2	48.2	6.7	23.0
PO_4^{3-}	mg/L	0.15	0.27	<0.10	<0.10	0.44	<0.10	<0.10	0.59	0.15	0.37
Total N	mg/L	3	<1	<1	<1	<1	<1	<1	11	2	5
Total P	mg/L	<0.10	<0.10	<0.10	<0.10	0.13	<0.10	0.10	0.20	0.48	0.13
F^-	mg/L	1.4	0.6	1.2	1.3	1.2	1.4	1.2	0.4	0.9	0.8
Li	µg/L	305	198	306	367	305	278	331	226	330	260
Mo	µg/L	200	<200	<200	<200	<200	<200	<200	<200	<200	<200
Ba	µg/L	10	194	9	9	17	10	12	103	90	75
Zn	µg/L	21	25	2	9	<2	<2	3	3	3	23
Al	µg/L	15	3	4	12	3	3	8	<2	4	3
Fe	µg/L	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
V	µg/L	8	8	3	4	15	4	3	9	8	16
Ni	µg/L	<2	6	<2	<2	4	<2	<2	105	<2	3
As	µg/L	4	<2	3	4	3	3	3	<2	<2	201
Co	µg/L	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Cu	µg/L	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Mn	µg/L	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Cr	µg/L	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Sn	µg/L	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Pb	µg/L	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Cd	µg/L	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Hg	µg/L	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	0.23

Note: DP# = Desalination plant number.

The chemical composition of SWRO brine is usually represented using only absolute values, which can lead to erroneous conclusions especially when multiple brines are listed together [56]. Introducing the chemical composition in percentage terms seems to be a more useful parameter to compare the chemical composition of different brines since it already takes into account the implication of the TDS value, which is related to the recovery rate of the desalination plant.

According to the results (Table 5), the ratio of the major ions in terms of the percentage of TDS remains remarkably stable regardless of the operating conditions (plant size, type of intake, pre-treatment, number of stages, etc.). Hence, a first approach method to estimate the brine chemical composition of any desalination plant located in the Canary Islands with standard feed conditions (seawater without a brackish water mixture) can be applied by multiplying their TDS by the ranges shown in Table 5. Furthermore, these values comply with the electroneutrality principle, which states that positive and negative charges must balance to zero.

In addition to the evaluation of the minimum/maximum concentration of specific parameters of potential interest, the last column of Table 5 can also act as a reference to identify possible anomalies in the case of a deviation from the established range, bearing in mind that such deviations could imply irregularities regarding the electroneutrality principle. Different brines found in the literature [21] perfectly fit within these ranges, whereas many other brines do not do so and also do not comply with the electroneutrality principle [56,57].

Table 5. Major ions in brine (as a percentage of total dissolved solids—TDS) per desalination plant (DP#) and global range per parameter.

Parameter	Unit	DP#1	DP#2	DP#3	DP#4	DP#5	DP#6	DP#7	DP#8	DP#9	DP#10	Range
Cl^-	% of TDS	54.80	55.33	55.58	55.53	54.59	55.08	54.84	54.35	55.56	55.58	**54.0–56.0**
Na^+	% of TDS	30.31	30.23	29.11	29.11	30.19	30.23	29.84	30.15	29.53	28.43	**28.0–31.0**
$SO_4{}^{2-}$	% of TDS	8.25	7.88	7.99	7.70	7.89	7.79	8.04	7.80	7.84	8.03	**7.0–9.0**
Mg^{2+}	% of TDS	3.62	3.58	4.21	4.31	3.95	3.75	4.16	3.76	3.87	4.13	**3.0–5.0**
Ca^{2+}	% of TDS	1.11	1.20	1.27	1.38	1.29	1.21	1.16	1.85	1.34	1.83	**1.0–2.0**
K^+	% of TDS	1.17	1.05	1.23	1.30	1.18	1.19	1.30	0.97	1.16	0.99	**0.9–1.5**
$HCO_3{}^-$	% of TDS	0.45	0.34	0.37	0.42	0.62	0.42	0.40	0.62	0.37	0.55	**0.3–0.7**
Br^-	% of TDS	0.19	0.25	0.20	0.20	0.19	0.28	0.22	0.23	0.21	0.28	**0.1–0.3**

In addition, an experimental correlation factor between electrical conductivity (µS/cm) and TDS (mg/L) was calculated for all the desalination plants. These results could allow a rough estimation of the TDS of a particular brine, knowing its electrical conductivity, which is a direct measurement.

The TDS/EC(@25 °C) conversion factor has been reported to lie between 0.5–0.9 for the majority of water types [58]. The same author indicates that the conversion factor will always be dependent on the specific chemical composition of the water. In this particular case study, salinities varying between 58,000–72,000 mg/L show conversion factors ranging from 0.73 to 0.76.

Interestingly, with respect to the different interconnections between the set of data and the operating parameters shown in Table 2, no significant differences were found between the plant production capacity or the different physical/chemical pre-treatments employed (including the use of antiscalants).

However, noticeable differences were found when separating desalination plants by type of intake. Several parameters show a difference in terms of the percentage of TDS, with a regular solid pattern observed across all the desalination plants. The exception was DP#7, with beach well water intake but showing similar characteristics to the open sea water group. Upon further investigation, it was realised that DP#7's beach well was constructed on artificial land. The fact that seawater was not in contact with natural land is the probable explanation as to why the DP#7 results are in the open sea water group instead of the beach well category (see Figures 4 and 5).

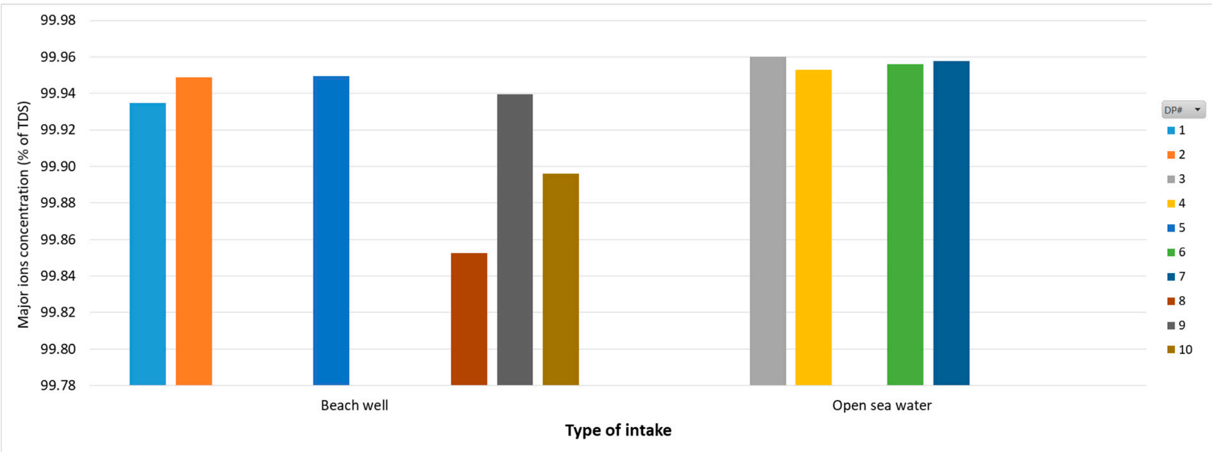

Figure 4. Sum of major ions in brine (as a percentage of TDS) per DP# by type of intake.

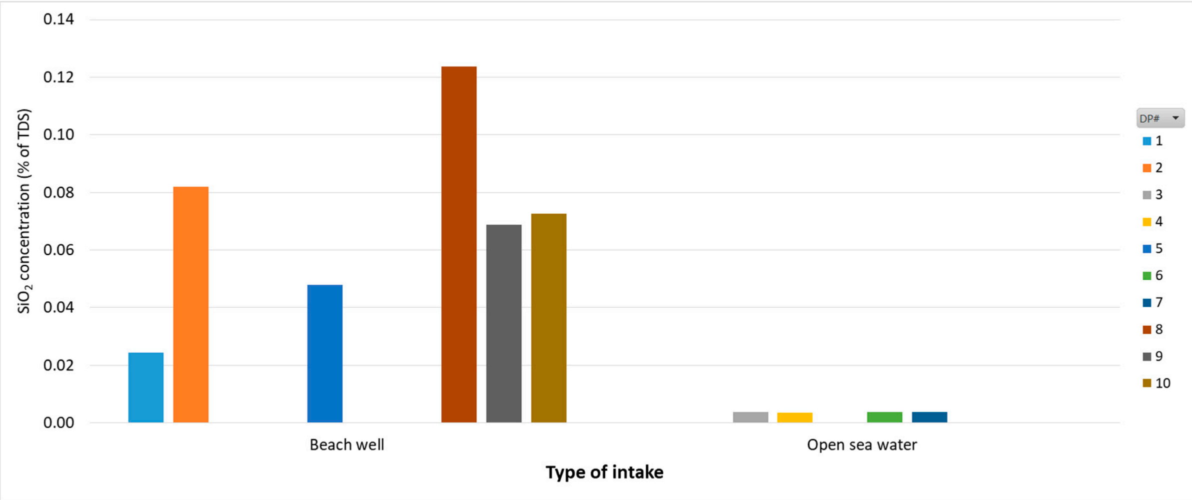

Figure 5. SiO_2 concentration in brine (as a % of TDS) per DP# by type of intake.

Percentages of the sum of major ions related to TDS. Open sea water intake desalination plants produce brines with a higher percentage of the sum of major ions (>99.95%) than beach well intakes (>99.85%). Values below that level (<99.85%) may be due to infiltrations of brackish water or contamination from other sources (waters with high levels of nutrients coming from agricultural land). These percentages could serve as a reference to verify the validity of the chemical analysis or even to detect any anomalies.

Percentage of silica (SiO_2) related to TDS. Notable differences were found between open sea water intakes, where there is no trace of silica (<2.41 mg/L), and beach well intakes, where the percentage of SiO_2 related to TDS can be around 0.02–0.13%, with absolute values of 15–80 mg/L. These high values can be attributed to the volcanic nature of the Canary Islands [59].

Other parameters with notable differences depending on the type of intake are nitrates, phosphates, vanadium, and barium, which are all higher in beach well intakes and total organic carbon (TOC), which is higher in open sea water intakes, as expected [60].

Special mention should be made of two particular cases, desalination plants (DP) 8 and 10. DP#8 corresponds to a beach well intake near agricultural land and DP#10 corresponds to a beach well intake with brackish water infiltrations, which explains the low feed conductivity (Figure 3) compared to the other nine plants. A higher level of calcium and strontium and a lower level of potassium were found in these two plants. Apart from these findings, the high levels of mercury and arsenic found in DP#10 can be linked to the proximity of a metallurgical industry and the proximity of the wastewater discharge to the seawater intake.

Further interesting results were found in terms of NaCl concentration. Since NaCl is the main product in terms of quantity that can be obtained from SWRO brine, and is a raw material for industrial applications such as the chlor-alkali industry, it is important to calculate its maximum amount in each SWRO brine. It is not uncommon to find SWRO brine TDS treated entirely as NaCl or the maximum quantity of NaCl calculated as the sum of chloride ion and sodium ion concentrations, potentially leading to erroneous conclusions. However, chloride ions are in excess of the stoichiometric ratio corresponding to the sodium ions present [61], even considering the sodium ions completely linked to chloride ions. The results corresponding to the last column of Table 6 are calculated taking into account both molar masses and the stoichiometric ratio.

Table 6. Difference between % NaCl and % sum of Na^+ + Cl^- per DP#.

	% Na^+	**% Cl^-**	**% Sum Na^+ + Cl^-**	**% Max NaCl**
DP#1	30.31	54.80	85.11	77.04
DP#2	30.23	55.33	85.56	76.84
DP#3	29.11	55.58	84.69	73.99
DP#4	29.11	55.53	84.64	74.00
DP#5	30.19	54.59	84.78	76.73
DP#6	30.23	55.08	85.31	76.84
DP#7	29.84	54.84	84.68	75.85
DP#8	30.15	54.35	84.50	76.63
DP#9	29.53	55.56	85.09	75.06
DP#10	28.43	55.58	84.01	72.27
		Overall Results		
	Sum of Na^+ and Cl^- $\approx$ 85% TDS		% max. NaCl $\approx$ 75% TDS	

Taking DP#6 as an example, with a brine TDS of 67,275 mg/L, the total amount of solids would then be 67.3 kg/m^3 brine. Considering the sum of both the chloride and sodium ions, this value decreases to 57.4 kg/m^3 brine. However, taking into account the above, the maximum quantity of NaCl would be 51.7 kg/m^3 brine. In this particular case, DP#6 daily brine production is 17,668 m^3/d. The difference between the two approaches would be a significant value of approximately 100 ton/d.

3.2. Strengths of Industrial DBV

Desalination brine valorisation has the potential to enhance the desalination industry economically, socially, and environmentally. Desalination brine is a resource that is available in huge quantities and can offer multiple advantages, which are covered in this section.

3.2.1. Environmental Impact Mitigation of Brine Discharge

Brine discharge into the sea creates diverse environmental impacts, including adverse effects on particular marine ecosystems and species sensitive to high salinity water such as the seagrass species *Posidonia oceanica* or *Cymodocea nodosa* [5]. Reducing or eliminating brine discharges (ZLD) would evidently mitigate or resolve the environmental impacts caused by it.

Applying so-called CCU technologies (Section 1.1) will also mitigate the environmental impact caused by CO_2 emissions. Furthermore, the recovery of minerals through a desalination brine treatment instead of current mining techniques could mitigate the environmental impacts produced by those processes [62].

3.2.2. Resource or Energy Recovery

Depending on the chemical composition of the DB, a significant number of chemical by-products can be obtained by applying different technologies (Section 1.1). Some, such as magnesium, have been classified as a critical raw material by the EU [48]. Certain by-products, especially liquid ones (NaClO, NaOH, and HCl), can even be used back in the desalination plant, avoiding the need to purchase them from external sources.

Reducing the importation of specific products, especially in the particular scenario of an isolated territory such as the Canary Islands, helps to reduce the influence of market instability, offering a major advantage to the local economy.

In addition, energy generation technologies based on the osmotic pressure gradient (Section 1.1) have the potential to offer a major advantage to desalination plants by reducing their energy consumption, the most important factor for their economic viability.

Desalination plants produce an enormous daily volume of brine as a by-product. Either by reducing energy consumption within the desalination plant or by producing a critical by-product with a high local demand, DBV applications can be highly beneficial.

3.2.3. Desalinated Water Production Increase

Increasing the fresh water production capacity while maintaining the feed intake or minimising the water intake needed to produce the same volume of fresh water by increasing the recovery rate is one of the main advantages of certain technologies, especially at the concentration stage (Figure 2). Furthermore, no extra pumping or intensive pre-treatment at the feed intake are needed since the brine is already available and will have passed through the pre-treatment stage.

This feature becomes of special relevance in the case of increasing fresh water demand where expanding the size of the plant is not possible. DBV applications would be the only solution to increase fresh water production in this scenario.

3.2.4. Hybrid Solutions—Zero Liquid Discharge (ZLD)

Instead of focussing on one particular technology, a number of investigations and projects consider a combination of various technologies, offering hybrid solutions able to outperform the efficiency of individual technologies. In some particular cases, the combination of already well-known technologies [63] can represent a major advantage compared to the limitations of emerging technologies. In other cases, hybrid solutions combining incipient with established technologies can offer a more robust solution [64], attaining a higher performance.

In the ZLD approach, the solutions that are proposed are based on a combination of different technologies with the objective of eradicating brine discharge and maximising water and resource recovery. Although there are currently several theoretical analyses [43,48] and ZLD solutions that have been applied for brackish water desalination plants [65] in inland locations where brine discharge is a complex issue, further developments need to be made to overcome the impacts and barriers corresponding to industrial DBV, especially when multiple technologies are used.

3.2.5. Potential Integration with Renewable Energies and Waste Heat

Most DBV projects consider the integration of renewable energies, waste heat, or even a combination of the two. Emerging technologies such as MD operate with a thermal energy benefit from using waste heat to raise the temperature of the brine to the correspondent temperature (40–80 °C) [44]. In this case, thermal energy is by far the main cost associated to the technology. Being able to use waste heat due to the relatively low temperatures involved can make the difference with regard to the economic feasibility of a project. However, for membrane technologies, the main cost associated to the processes is usually that of electric energy consumption. Solutions that can couple wind or solar photovoltaic energies will lower their carbon footprint.

Coupling DBV technologies with renewable energies would undoubtedly reduce the associated environmental impact produced by the extra energy consumption required.

3.2.6. New Employment/Business Opportunities

A robust brine desalination industry can also generate local economic development through the commercialisation of new products and the creation of multiple new jobs. A whole new sector that encompasses different job areas (engineering, R&D, maintenance, sales, marketing, etc.) can be created, fostering in addition specialised education/training in regional universities and technological centres for students and workers who would like to work in this field.

New business opportunities could also arise as a result of innovative synergies between different sectors/industries (energy, chemical, water, research institutions, etc.). The development of successful DBV applications could help new companies to establish themselves or old ones to thrive.

3.3. Impacts and Barriers of Industrial DBV

Besides the numerous potential strengths associated to DBV applications, it is important to examine the expected impacts and the actual barriers once projects upscale to an industrial level. This information is especially relevant to companies developing a technology which they would like to implement within the desalination industry.

3.3.1. Pre-Treatment

The extreme importance of an optimum pre-treatment stage for any brine valorisation technology cannot be stressed enough. Several technologies have proven successful when using artificial brine as the input solution, but their performance is compromised when using real brines. An optimum pre-treatment is key to obtaining the purest brine possible and, therefore, increasing the efficiency of any brine valorisation technology. Consequently, the pre-treatment selected must be efficient, have a low energy consumption, be sustainable and environmentally friendly, and, ideally, minimise the generation of residues.

A brine valorisation technology without a solid and well-defined pre-treatment stage can lead to wrong conclusions in terms of the general success, overall performance, energy consumption, and environmental impact.

Membrane technologies in particular are highly susceptible to a noticeable loss of performance as a result of inorganic, organic, and colloidal fouling and biofouling [66]. Due to the inherent increase in the brine concentration in most valorisation processes, both fouling and scaling are critical barriers that need to be overcome, either by selecting an optimum pre-treatment or by the development of new membranes less prone to the problem of fouling/scaling [67].

It is also important to take into account the chemical products added in the pre-treatment stage of the desalination system, especially if antiscalants are used. Certain valorisation processes, including chemical precipitation (CP), can be negatively affected by the presence of antiscalants, and solutions that may work well in desalination plants with no chemical pre-treatment could fail under altered circumstances.

3.3.2. Technology Readiness Level of Emerging Technologies

When it comes to evaluating the sets of results obtained by different technologies, it is necessary to assess their technology readiness level (TRL) in order to verify the degree of certainty applied to specific requirements, such as the scale of tests, repeatability of results, variety of conditions examined, type of brine, etc.

Depending on their TRL, some processes would need more investment to, for example, continue with lab research, build a pilot plant, test the pilot plant under real conditions, or develop a marketing plan for their technology.

In a number of instances, technical limitations arise in brine valorisation processes during the scale-up of the technologies. Exciting results may be obtained in the laboratory under controlled conditions using artificial brines, but the performance may decrease as the TRL increases and actual desalination brines are used. The results obtained in different projects [68,69] are illustrative examples of this type of barrier.

3.3.3. Environmental Impact

DBV processes can generate various environmental impacts, starting with the negative impact of their usually high energy consumption, especially when the required energy is generated by fossil fuels. In a number of cases, the developments which were conceived with the idea of minimising environmental impacts, such as avoiding brine discharge, could nonetheless result in other severe environmental impacts such as increasing CO_2 emissions due to a higher specific energy consumption (SEC) or the generation of extra residues, including precipitates with no commercial value or cleaning chemical agents.

Numerous processes, including CP and BMED, typically generate low purity or low concentration products, requiring an additional purification or concentration step which involves higher energy consumption (high carbon footprint). Likewise, technologies such as ion exchange resins, produce highly concentrated residues during the regeneration process.

Certain brine valorisation techniques associated to the Solvay method used for CCU emit more CO_2 to the atmosphere than the volume captured due to the high energy consumption involved in the regeneration of the reactants used in the process.

Moreover, brine concentration techniques are applied to increase the overall water recovery of a desalination process, generating more fresh water and an even more concentrated brine. If this brine is not further processed and discharged into the sea, it can aggravate the negative impact on the marine environment at the discharge area due to its increased salinity.

Another issue concerns the possible use of hazardous/harmful materials in DBV technologies. For instance, although the use of mercury cells in the chlor-alkali electrolysis process has decreased over the years, they continue to pose a danger to both human health and the environment [70].

3.3.4. High Capex/Opex

One of the main goals of any brine valorisation process is to minimise as much as possible its energy consumption, which usually corresponds to the principal contributor to the overall cost. Despite the development of new techniques and a significant reduction in recent years in energy consumption values (<10 kWh/m^3), especially compared to classic thermal solutions (up to 70 kWh/m^3), in many cases it remains a key obstacle to economic feasibility [71].

In general, the main associated running cost to most DBV technologies is their specific energy consumption (SEC), and it is therefore of vital importance to evaluate this parameter. It should be noted that the SEC is sometimes calculated in reference to the volume of brine treated (kWh/m^3 of brine) and sometimes to the kg of product generated (kWh/kg of "product") [72].

Morgante et al. [45] undertook a thorough techno-economic analysis of different DBV solutions. The brine treatment specific cost factor for their MLD system was 8.49 EUR/m^3 but fell to −0.02 EUR/m^3 when taking into account THE revenue from by-products. Other DBV options, also including possible by-products revenue, were in the range of 0.06–0.96 EUR/m^3 [45].

The extent of the brine valorisation solution chosen in terms of water recovery will also have a massive influence on the economic impact. For instance, in a study [60] comparing an MLD system comprising RO + FO and a ZLD system including RO + FO + BC (Brine Concentrator) + BCr (Brine Crystalliser), it was determined that the MLD system would obtain a recovery rate of nearly 85% at a SEC of 5.4 kWh/m^3, whereas the ZLD would obtain a recovery rate of 98% at a SEC of 10.4 kWh/m^3, which is practically double but to generate just 13% extra product water.

Furthermore, numerous processes related to the different phases of a brine valorisation technological solution require the addition of chemical products, especially in some pre-treatment processes, including CP and CCU, or certain concentration steps (e.g., electrodialysis metathesis (EDM)). If these reactants are not obtained in other steps within the overall brine valorisation process, their implicit cost needs to be considered along with their supply and storage and the possible need for dosing pumps.

Another important factor to be considered is the residence time in the particular cases where chemical reactions take place. Depending on the volume of brine selected to be treated, a high residence time will have a significant influence on equipment selection and the surface area needed to complete the reaction. For instance, a high residence time would seriously hamper the treatment of the full volume of brine generated due to the accumulation produced by the extra time required for completion of the reaction.

3.3.5. Legal Restrictions

Legal constraints concerning any part of a brine valorisation process can suppose a major barrier to its full development. For instance, one of the main limitations regarding brine valorisation technologies aiming to generate electrical energy based on the salinity gradient power between brine and wastewater is the prohibition in many countries to reuse water which has previously been in contact with wastewater as fresh water for human consumption. Despite chemical analyses [73] showing compliance with the legal limits, the current legislation in countries such as Spain (RD 1620/2007) does not contemplate the use of this water for human consumption, jeopardizing the economic viability of such processes.

However, in 2017, the World Health Organization (WHO) published a document titled "Guidance for producing safe drinking-water" [74], which reported various successful cases of the reuse of wastewater as drinking water in Singapore, Namibia, the USA, Australia, and South Africa. Therefore, in certain cases, barriers may come from legislative elements. Significant changes concerning this type of water reuse could transform the overall brine valorisation scenario, leading to a real advantage in terms of the economic viability of certain technologies (PRO, RED), promoting their development, and playing a major role in the Circular Economy Action Plan [14].

3.3.6. Limited Available Research Data

Emerging technologies and novel processes make up a high percentage of the brine valorisation research. The majority of the research articles focus on proving the technical viability of their proposals, generally using an artificial brine with a particular chemical composition simulating an already pre-treated desalination brine and without undertaking any economic analysis. One of the most repeated statements in the conclusions of these articles refers to the need to continue relevant research, either by using brine with different characteristics or real brine, varying operating conditions as well as reactants, testing different energy inputs, increasing the scale, etc.

Even the suppliers of products already in the market, such as nanofiltration and FO membranes, or other technologies with advanced TRLs (8–9) are eager to find collaborations where their products can be tested under different conditions, thus increasing the set of available research data to be able to improve their development, gaining versatility and robustness.

The level of confidence in emerging technologies is usually directly related to the amount of research data collected, and this can be negatively affected due to a lack of information regarding economic, energy, or exploitation factors. This barrier compromises the possibility of investment from key members of the industry in these emerging technologies and, consequently and simultaneously, complicates the gathering of the amount of research data required.

A key factor to be able to achieve the desired progress concerning DBV technologies and processes is research continuity. Therefore, it is vital to continue to develop new technologies, improve specific elements such as membranes or new materials, increase the experimental data available, build new pilot plants, and arrange collaboration agreements between technology providers, research facilities, and desalination plants.

3.3.7. Commercialisation of By-Products

Brine valorisation processes through the generation of chemical by-products need to confront the challenge of penetrating the existing market for those products, considering the local demand and the degree of purity of those products already in the market.

For instance, after a brief investigation carried out in the Canary Islands, sodium hypochlorite (NaClO) was found to be the most important by-product for the local economy. To a lesser extent, sodium hydroxide (NaOH), hydrochloric acid (HCl), and sodium bicarbonate ($NaHCO_3$) are the other by-products with the potential for commercial success. As most other by-products would have to be exported, a different approach would be required. A DBV technology which produces magnesium hydroxide, $Mg(OH)_2$, and calcium carbonate, $CaCO_3$, for instance, may be successful in some parts of the world but less so in other places where there is no demand for such products.

In some cases, technological advances offer solutions and by-products that are difficult to place in an established market. For instance, processes that aim to reduce to zero desalination brine discharge and at the same time produce sea salt need to take into consideration the enormous amount of products generated. This typically amounts to around 60–70 kg of solids for each cubic meter of brine, meaning 2.5–3.0 kg of salts hourly for each cubic meter of brine treated. So, taking as a reference a medium capacity desalination plant of 5000 m^3/d fresh water with a 45% recovery rate, treating all the volume of brine generated (6111 m^3/d) to completely eliminate its discharge would produce around 400 ton/d of solids. This would in turn mean the need for a huge area for storage, complicated logistics and transport requirements, along with extra purification systems to be able to compete in the existing market. Following the same reasoning, this could be applied to any mass production of any chemical (e.g., the huge volumes of diluted NaOH and HCl produced by BMED).

Furthermore, in a number of instances, there are noticeable discrepancies regarding the exact composition of the generated by-products. Of the few articles that do provide a detailed chemical composition, reference [75] shows the different precipitation phases of diverse compounds related to the different values of pH and temperature. Not taking into account the various complexes involved within the precipitation processes or the purification methods needed to be able to commercialise the product can lead to erroneous conclusions.

3.3.8. Lack of Specific Materials/Components

The optimisation of new processes concerning brine valorisation also depends on the development of new materials and products, specific to this target. A clear example would be the development of particular membranes for different processes such as NF, FO, MD, or the different types of electrodialysis. Such membranes started life as modified versions of RO membranes, although there has been gradual progress in adapting them to explicit technologies. However, more research is needed to fully adapt the membranes to their purpose, maximise the efficiency of the overall process, increase the flux, and reduce fouling problems.

Other cases where the need for more R&D into new specific materials is evident include: different electrodes in electrolysis processes, where new electrodes can enhance a favourable reaction compared to the present situation where the opposite occurs [30]; new materials for adsorption reactions for lithium recovery processes [76], and chemicals used as solvents for liquid–liquid extraction processes [77]. New materials or components tend to imply a higher economic expenditure, which could compromise the viability of the process.

3.3.9. Lack of Specific Simulation Software Tools

The novel nature of the majority of DBV processes makes it difficult to develop appropriate simulation software tools, which would allow an easier and faster evolution of the multiple processes involved. Being able to optimise the different parameters or configurations in a projection could enhance the quantity and, importantly, the quality of the results obtained physically. However, no simulation software tools have been detected in the literature by the authors of the present paper.

An initial evaluation has been used to highlight the most critical barriers/limitations for the industrialisation of DBV processes detailed in this section. Likelihood and impact of the nine barriers/limitations identified in Table 3 have been evaluated quantitatively and given, in each case, a score between 1 and 5, shown in Table 7. The product of the two aspects show the overall relevance of each factor.

Table 7. Evaluation of the likelihood and the impact of a list of identified barriers for DBV industrialisation.

Barrier	Likelihood-Value		Impact-Value		Total
Pre-treatment	Most technologies need an exhaustive pre-treatment	4	Lack of a proper pre-treatment will directly reduce performance in practically any DBV process	4	**16**
TRL of emerging technologies	Practically all DBV technologies have a low-medium TRL	5	Risks associated to non-commercially tested technologies will reduce their chance of success	4	**20**
Environmental impact	Emerging technologies are usually conceived with a so-called "green thinking" approach and harmful substances tend to disappear from all DBV processes	2	Processes with a high associated environmental impact will not be given the chance to progress	5	**10**
High Capex/Opex	Most DBV technologies will have high material and operating costs	4	The question of economic viability will always be a determining factor. It may be compensated by revenues from by-products or energy	5	**20**
Legal restrictions	Although it is a matter of concern, its likelihood is very low and limited to particular cases	2	These restrictions may stop/delay the development of a process	4	**8**
Limited available research data	Especially data related to pilot plants with real brines	3	The process of obtaining trustable data is a long one, thus delaying the commercialisation of any DBV solution in the short term	3	**9**
Commercialisation of by-products	Most DBV processes end up generating by-products	4	A process that generates non-marketable by-products will fail, as they will become more waste	4	**16**
Lack of specific materials/components	Emerging technologies usually need new materials/components in order to be optimised	4	Mostly needed to increase performance and to overcome common barriers	3	**12**
Lack of specific simulation software	No specific software has been developed as far the authors are aware	5	It would increase with the speed of the R&D process	2	**10**

Low TRLs of emerging technologies and high Capex/Opex of DBV technologies are presented as the most challenging barriers for their industrialisation, as well as the need for an exhaustive pre-treatment and the generation of marketable by-products.

4. Conclusions

In this study, a total of 10 heterogeneous desalination plants located in the Canary Islands were selected to collect brine samples and obtain a physicochemical characterisation (37 parameters analysed). The aim was to improve the knowledge about brine chemical composition and its correlation to certain operating parameters. It was found that, as a percentage of TDS, the major ions fall within a stable and narrow range (55% Cl^-, 29.5% Na^+, 8% SO_4^{2-}, 4% Mg^{2+}, 1.5% Ca^{2+}, 1.2% K^+, 0.5% HCO_3^-, and 0.2% Br^-), irrespective of the desalination plant location or characteristics, complying with the electroneutrality principle. The most significant characteristic found was the type of intake. Open sea water intakes were found to consistently generate brines with a higher percentage of major ions and a higher level of TOC than beach well intakes, the brines of which in turn have higher amounts of silica, nitrates, phosphates, vanadium, and barium. Interestingly, the conversion factor between TDS and electrical conductivity (@ 25 °C) resulted in a tight range of 0.73–0.76.

A continuation of this study and confirmation of the results obtained could be highly beneficial to any DBV technology provider or user, allowing them, for example, to consider an initial approach to the chemical composition of a particular brine simply by knowing its electrical conductivity. In addition, any significant deviation from the ranges calculated for each parameter could also serve as a warning flag to identify possible anomalies in the desalination plant.

In conjunction with the physicochemical characterisation study, various impacts of and barriers to the industrialisation of brine desalination treatments were identified. The technology readiness level (TRL) plays an important role in the evaluation of both the technical and economic feasibility of emerging technologies immersed in a process of continuous evolution and optimisation, often with the need to develop new materials and reduce the specific energy consumption. High Capex and Opex values also need to be compensated with revenues from the commercialisation of by-products obtained, which need a specific concentration, purity, and demand to enter the market. The environmental impact caused by brine valorisation technologies takes special relevance in an age in which climatic change is one of the biggest dangers that the world faces. The carbon footprint of any process needs to be reduced to a minimum through the use of renewable energies whenever possible.

This evaluation and the future development of this work, such as the elaboration of a more comprehensive decision matrix evaluating the observed factors for several technologies, could become a powerful tool for the comparison of different DBV technologies and provide a clear roadmap for their development.

Nevertheless, it seems clear that the foundations on which the future of desalination brine valorisation will be built are robust enough for fully developed technological options to start their appearance in the market in the near future, with sustainable and economically feasible solutions, probably suited for the particularities of each desalination plant since a one-fits-all approach does not seem to be feasible.

Perseverance, continuous improvement, research continuity, and investment in the development of new materials and pilot plants to enable the gathering of more research data will determine the success of the technologies related to desalination brine valorisation.

Author Contributions: Conceptualization, Á.R.-F., B.P.S. and N.M.-M.; methodology, Á.R.-F., B.P.S. and N.M.-M.; validation, Á.R.-F., B.P.S. and N.M.-M.; formal analysis, Á.R.-F. and B.P.S.; investigation, Á.R.-F.; resources, Á.R.-F.; data curation, Á.R.-F.; writing—original draft preparation, Á.R.-F.; writing—review and editing, Á.R.-F., B.P.S. and N.M.-M.; visualization, Á.R.-F.; supervision, B.P.S. and N.M.-M.; project administration, B.P.S.; funding acquisition, B.P.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research and APC were co-funded by the European Regional Development Fund (ERDF), INTERREG MAC 2014-2020 programme, within the E5DES project (MAC2/1.1a/309).

Data Availability Statement: Data are contained within the article.

Acknowledgments: The authors would like to thank the Cabildo of Gran Canaria–Sociedad de Promoción Económica (SPEGC) for its support within the SEIDI agreement signed with the Ministry of Science and Innovation–Government of Spain. The authors also acknowledge the contribution of the technical staff of the Canary Islands desalination plants included in this brine characterisation study.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

BC	Brine concentrator
BCr	Brine crystallizer
BMED	Bipolar membrane electrodialysis
BMSED	Selectrodialysis with bipolar membranes
CCU	Carbon capture and utilisation
CP	Chemical precipitation
DB	Desalination brine
DBV	Desalination brine valorisation
DP	Desalination plant
EC	Electrical conductivity
EDM	Electrodialysis metathesis
FO	Forward osmosis
FTIR	Fourier-transform infrared spectroscopy
HPLC	High-performance liquid chromatography

HPRO	High pressure reverse osmosis
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma-optical emission spectrometry
IEx	Ion exchange
MCr	Membrane crystallisation
MD	Membrane distillation
MED	Multi-effect distillation
MLD	Minimal liquid discharge
MSF	Multistage flash distillation
NF	Nanofiltration
OARO	Osmotically assisted reverse osmosis
PRO	Pressure retarded osmosis
RED	Reverse electrodialysis
SWRO	Seawater reverse osmosis
RO	Reverse osmosis
SD	Spray drying
SEC	Specific energy consumption
SED	Selective electrodialysis
TDS	Total dissolved solids
TOC	Total organic carbon
TRL	Technology readiness level
TSSE	Temperature Swing Solvent Extraction
VCD	Vapour compression evaporation
ZLD	Zero liquid discharge

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