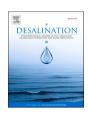


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The economic value of the extracted elements from brine concentrates of Spanish desalination plants

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HIGHLIGHTS

- The value of the elements present in the desalination brine has been obtained.
- This value varies depending on the source of desalinated water.
- Two types of valuable elements are identified according to price and quantity.
- The results are key to design the brine mining strategy.

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ABSTRACT

The disposal of desalination brine, which contains a higher concentration of salts, is treated as waste and discharged into the environment. In this brine, several elements, when processing and extraction were possible, could be susceptible to exploitation and valorisation. Among all the ions existing in desalination brine, and whose industrial use is possible, sodium (Na), magnesium (Mg), calcium (Ca) and boron (B) are found at high concentrations; there are also other elements, not as abundant as previous, but highly demanded in the current industry, such as lithium (Li), rubidium (Rb), strontium (Sr) or gallium (Ga). These elements, as well as other alkaline metals, have taken on considerable prominence today due to their technological applications. Analysing the prices and quotations of these elements in the international markets for raw materials, it is possible to determine the economic potential of this mining activity of desalination plants in Spain. The economic value of the extracted elements also incorporates other additional advantages, which focus on the elimination, or reduction, of brine discharges, the savings in transportation and transaction costs of raw materials, in addition to the considerable reduction in environmental impacts caused by traditional mining.

1. Introduction

Water desalination is a valuable source of water resources in a context of freshwater scarcity and saltwater availability [1,2]. Current expectations are for increasing water scarcity and, consequently, increases in desalination in the coming years [3,4]. This expected increase in desalinated water production will be associated with a worsening of its environmental impacts, which are centred on emissions from energy consumption and discharges of the salt concentrate produced during desalination, including heavy metal pollution [5–7]. In other words, this salt concentrate generated in the production of desalinated water is

generally treated as a waste and consequently discharged into the marine environment. However, it should be borne in mind that this salt rejection contains a considerable number of elements which, if it were possible to process and extract them, could be exploited within the framework of the circular economy. In this way, not only would an environmental impact derived from temperature, salinity, and the presence of pollutants in the dumped concentrate be avoided [8–11], but an added productive value would also be obtained [12,13]. Therefore, by recovering these elements, we manage to reduce the negative impacts of the dumping of these rejects and obtain materials with industrial applications, minimising damages to the environment.

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Firstly, with the aim of focusing the study on the most abundant elements in the rejects from desalination and considering those that are most profitable from the point of view of their use, the classification carried out by Kumar et al. [14] stands out. These authors analyse the economic viability of extracting different elements, among which we should highlight some that are very abundant, such as sodium (Na), magnesium (Mg) and calcium (Ca); as well as others that are not very abundant, although in great demand in today's industry thanks to their technological applications, such as lithium (Li), rubidium (Rb) or strontium (Sr).

These conclusions are in line with Ortiz-Albo et al. [15], who consider the main factors involved in the techno-economic feasibility of extracting some of these and other minor elements, such as boron (B), bromine (Br), caesium (Cs), gallium (Ga), germanium (Ge), indium (In), or uranium (U). For these authors, Br is well-established at industrial scale and the positive results obtained in the profitable analysis could be considered to extend their production from desalination brines, while Cs, In and Rb were pointed as promising metals to upgrade their extraction technologies from brine concentrates to reach the industrial level thanks to their high positive market trends. Similar conclusions hold true for U, whose extraction technology has been one of the earliest considered, but more research has to be performed on U separation to extract this element from high salinity concentrates.

The possibility of obtaining certain inputs from salt concentrate from desalination is conditioned by a series of technical and economic restrictions that must be taken into account. Obtaining these materials is not simple and requires complex physicochemical processes, which can follow specific schemes based on information on the value of these resources and the cost of their extraction. This is the reason to review the state of the art and the existing literature to date, in an attempt to explore this technical and economic feasibility. However, some of these technologies are currently being evaluated and the analyses are restricted to laboratory scale, which implies that industrial scale analyses have not yet been carried out [16]. On the one hand, most common

Table 1Summary of the main resource recovery processes.

Categorization	Technical process	Elements (reference papers)	Major challenges of recovery techniques
Electrochemical	Electrodialysis and membrane electrodialysis	B, Li, Ca, Mg and Br [18–20]	Fouling of membranes, high costs, less stability in extreme conditions and shorter membrane lifespan
	Capacitive deionization	Li, Ca, Mg and Na [21,22]	Longer regeneration time for electrodes and deterioration of adsorption capacity over time
	Electrochemical batteries	Li [23,24]	Less stability of electrodes
Physiochemical	Adsorption/ desorption	Most minerals [22,25,26]	Insufficient adsorption capacity, costly due to the requirement for large quantities of chemicals
Thermal	Membrane distillation and membrane distillation crystallisation	Ca, Mg, Rb, Na, S, Li, Ba and Sr [25,27,28]	Low permeate flux, high energy requirements, fouling of membranes
Pressure driven	Nanofiltration	Li, In and Ge [29,30]	High energy requirements, shorter membrane lifespan due to the high- pressure gradient, crystallisation of salts

technical processes used to extract minerals are listed in Table 1, in accordance with the classification and findings of Ihsanullah et al. [17] and other specified references.

On the other hand, Zhang et al. [22] develop an economic comparison of different recovery approaches and cost analysis of desalination plants, showing advantages and disadvantages among membrane distillation (less brine disposal and higher crystal quality, but higher energy cost due to external heat required and relatively low production capacity), electrodialysis (electrical energy is the only energy operational cost, minerals recovered with high purity and energy can be recovered as well, but additional cost of pre-treatments is required and maintenance cost of membranes could be significant) and adsorption/ desorption (relatively lower operational costs than other processes but lower revenue than other processes, only profitable for high value minerals). Despite the high cost of these brine resource recovery approaches, it is anticipated that future technological developments will allow for significant cost reduction [17], which could help to put in balance costs and revenues of the entire process and make the difference between one method or another.

It is true that the cost of the technology required for a given extraction can sometimes prevent the use of an element from being profitable, as the quantities obtained are not very high [31]. In this sense, it is worth noting that exploring new cheap methods to achieve the extraction and use of these new resources, with high-energy efficiency, can contribute to improve the feasibility of the whole process. Some key aspects to guarantee their financial viability are the price of the extracted element and the full cost of the technology that must be used for its extraction, both for installation and maintenance, with the energy cost being particularly relevant in this regard. In this vein, recent studies have shown that advances in the use of solar or wind energy can counteract this effect, improving their production costs and efficiency

According to Zhang et al. [24] and in line with the study by Zhao et al. [20], electrochemical battery technologies represent a cost-effective and rapidly developing field of research for the recovery of lithium from salt lake brines, where lithium is abundant [33], and seawater. The low cost of raw materials and low energy consumption make the electrochemical battery method more economical and promising. Zhang et al. [24] also stress that future research on this technology should focus on developing new battery systems with high reversibility and low operating cost for large-scale industrial applications, for which electrochemical battery technology shows great potential [23].

Other factors involved in the financial feasibility [15] are the market trend, essential to make the extraction of the element attractive and profitable (which is conditioned by the availability of the element and its potential use), the risk associated with their discharge (for ecosystems or human health), or the relevance for their industrial use (depending on the state of the art of the necessary technology). Major uses of minerals that can be recovered from seawater brine could be seen in Ihsanullah et al. [17], Loganathan et al. [25], Ortiz-Albo et al. [15], and Zhang et al. [34], where main markets and distribution channels facilitate their trade as components of new batteries, glasses, lubricants, pharmaceutical products, aeronautics, ceramics, textiles, chemical and construction industries, soil amendment, fiber-optics, laser technologies, fertilizers and pesticides, soap and detergents, fire retardants, fireworks, well-drilling fluids, petroleum additives, lighting or nuclear industry.

The study of Kumar et al. [6] focus on the sustainability determinants of brine mining and authors believe that future research should be directed toward the following objectives to support wider commercialization of these recovered resources: further improvement of adsorbents to enhance selectivity and rapid uptake toward the desired ion, development of novel electrochemical methods for capture of a desired metal, engineering of adsorbent configurations to maximize adsorption efficiency and to facilitate the regeneration process, integration of adsorbent and membrane processes, and detailed techno-economic assessment of potential recovery process with consideration of

extraction costs and generated revenues, particularly in comparison to the present decoupled business cases for existing brine disposal techniques and land mining to extract these resources.

For its part, Sharkh et al. [35] considered only those chemical substances appearing on the right-hand side of a figure (NaCl, Br, Mg, K, Ca, Li, Sr, Rb, and B) which shows the combination of price and availability of elements present in Arabian Gulf seawater and where economic viability criteria of Kumar et al. [14], Loganathan et al. [25], and Shahmansouri et al. [36] were reflected together. Sharkh et al. [35] state that the most important technologies for economic use of products from brine concentrates are technologies for more economic separation (as nanofiltration, with the least possible input of energy and reagents) and technologies for more economic concentration (with rapid advances in osmotically-assisted reverse osmosis technology, which allow the application of low-energy membrane-based methods of concentration to ever more concentrated brines).

Based on the above and given the problems posed by discharges from increasing desalination and the possibility of extracting valuable elements from the salt concentrate generated during the process, the main objective of this article is to study the economic value of the extracted elements described above, after considering the characterisation of water analysis in the area of study, Spain. This will make it possible to determine the economic potential of brine mining; specifically, what the value of the extracted elements is, which should help us to estimate what we are willing to pay by investing in extraction technologies to obtain benefits from this operation. By considering the value of the final elements, as feasibility of extraction is highly dependent on commodity pricing [36], it would be possible to develop a framework of operational research strategies with the aim of valorising desalination rejects.

2. Data and methodology

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In terms of methodology, the development of the research is based on the search, price analysis and values on international raw materials markets of the elements in the rejects from desalination plants that can be commercially exploited. In this sense, sodium (Na), magnesium (Mg), calcium (Ca), lithium (Li), rubidium (Rb), strontium (Sr), boron (B) and gallium (Ga) have been considered. This choice is based on income potential one of the factors that determine the viability of this mining activity.

The production capacities of each plant and the volume of reject water with which it can operate must also be considered. There is a consensus on the production of desalinated water that implies a 1:1 ratio, i.e. one unit (cubic metre) of reject water is produced for each unit of desalinated water. The production capacity of each facility will result in a capacity to extract the elements contained in the reject concentrate.

2.1. Selection of elements

There are many materials present in the water captured by desalination plants. Some of them can be very valuable, as is the case of gold (Au), but they are present in very small quantities, below one part per trillion (ppt) or 1 ng/L (nanogram per litre), which makes it practically unfeasible to consider them for commercial exploitation analysis.

The composition of the water captured by desalination plants varies depending on their geographical location. Contingent on the degree of salt concentration or mineralisation of the water, different proportions of elements can be found in the dry residue. For our research, we have taken the values obtained in the samples of the reject water from the desalination of nine plants located in different parts of Spain. The origin of these resources is brackish groundwater and seawater from the Atlantic Ocean and the Mediterranean Sea. Different desalination technologies such as reverse osmosis, multi-stage flash, or electrodialysis may produce brines with different compositions. All the desalination plants contemplated in this study apply reverse osmosis to remove salt from seawater or from brackish water. The composition of the reject

water from these locations differs slightly in most of the materials, but there are certain elements of high commercial value, such as lithium (Li), which is found more abundantly in the reject water of brackish groundwater desalination plants.

The Atlantic Ocean desalination plant of this study is located in the Canary Islands with a daily water production of some $30,000~\text{m}^3$. The desalinated water obtained produces approximately the same volume of brine water. The Mediterranean Sea desalination plants are located in the Balearic Islands and the Spanish Mediterranean coast with a daily water production in the range of $7000-210,000~\text{m}^3$ and the same volume of brines. Finally, the brackish groundwater desalination plant is located in southeast Spain, with three different location wells and a daily water production in the range of $3000-18,500~\text{m}^3$, and the same volume of brines.

The most abundant elements present in desalination reject water, as shown in Table 2, are chlorides and sodium, which account for 86-87~% of the dry residue of desalinated seawater rejects, and 63~% of the dry residue of rejects from brackish groundwater plants. However, their economic potential is smaller. It is only possible to consider the commercial value of sodium (Na) given its abundance, accounting for 27~%-48~% of the dry volume of all elements present in plant reject water, and the potential for its applications in industrial markets.

Apart from the case of sodium, the volume of elements that could be considered for some commercial use represents only 4 %–8 % of the total dry waste from desalination plant reject water.

As we can see, chlorides (Cl) and sodium (Na) are the most abundant elements present in the reject waters. There is also a notable presence of sulphates (SO₄), but unless they are combined with another element that has a commercial application, they do not stand out for their commercial value. There are a series of elements of interest that are detected, but in very low concentrations, with a presence of below 1 g/m³, such as barium (Ba), molybdenum (Mo), vanadium (V), indium (In), rubidium (Rb) or scandium (Sc). At these concentrations, despite the high prices of these materials, it is not possible to consider an analysis for their commercial exploitation. The exception is rubidium (Rb) which, given its exorbitant price, is of some commercial interest despite its low concentration.

Deciding which elements are worth recovering from desalination plant brines requires the consideration of several factors, including the concentration of the element in the brine, the market demand for the element, the price of the element, the cost of recovery, and the environmental impact of recovery. In this part of the research, we consider only the concentration and the price of the elements present in the brine. The results will help to promote research in other areas of the project to advance the techniques and procedures for the extraction of elements by identifying the elements with high-income potential and focusing the efforts on the most valuable choices.

Among the most valuable elements present in the reject concentrate, the most abundant, apart from sodium (Na), would be magnesium (Mg) and calcium (Ca), which represent 74 %–90 % of the total value of the set of elements that can be commercially exploited.

In addition to these most abundant elements, with commercial and industrial applications, there are a series of elements in low concentrations but with a very high market value. Therefore, the selection of elements, shown in Table 3, has been carried out based on their level of concentration in the brine reject waters.

With this selection of elements (Table 3 and Fig. 1) that are present in the reject flow of desalination plants, it is possible to carry out the economic analysis of the exploitation potential of the different locations and water abstractions.

The economic analysis must consider the levels of efficiency of extraction of different elements and materials. The element recovery uses a wide variety of different laboratory techniques [37]. It is not possible to replicate the main laboratory conditions in an industrial-scale process. It is not always possible to achieve 100 % efficiency in the extraction of materials. Levels in the range of 50 %–70 % can be

Table 2 Composition of desalination plant reject water. Source: own elaboration based on analytical data from nine facilities in different locations. Samples taken in September 2022. Figures in kilograms per cubic metre (kg/m^3).

Elements (identified species)	Atlantic Ocean	Mediterranean Sea	Brackish groundwater	Average	Standard deviation
Aluminium (Al ³⁺)	0.001	0.001	0.001078	0.00103	0.000045
Ammonium (NH ₄)	0.0001	0.0001	0.00025	0.00015	0.000087
Silicon (SiO ₂)	0.011	0.015	0.05	0.02533	0.021455
Barium (Ba ²⁺)	0.00005	0.0005	0.0005	0.00035	0.000260
Bicarbonates (HCO ³⁻)	0.253	0.273	0.851	0.45900	0.339629
Carbonates (CO ²⁻)	0.02	0.02	0.02	0.02000	0.000000
Boron (B)	0.006647	0.008921	0.00479	0.00679	0.002069
Calcium (Ca ²⁺)	0.717	0.826	1.554	1.03233	0.455052
Chlorides (Cl ⁻)	15.568	36.065	13.866	21.83300	12.354617
Strontium (Sr ²⁺)	0.014	0.026	0.04	0.02667	0.013013
Fluorides (F ⁻)	0.0021	0.0025	0.0025	0.00237	0.000231
Phosphates (PO ₄ ³⁻)	0.00016	0.00016	0.000722	0.00035	0.000324
Hydroxide (OH ⁻)	0.00016	0.016	0.00016	0.00544	0.009145
Iron (Fe ²⁺)	0.0001	0.0001	0.002814	0.00100	0.001567
Magnesium (Mg ²⁺)	2.143	2.271	1.58	1.99800	0.367613
Manganese (Mn ²⁺)	0.0001	0.00001	0.0001	0.00007	0.000052
Nitrates (NO ³⁻)	0.0005	0.0029	0.456	0.15313	0.262293
Nitrites (NO ²⁻)	0.00001	0.00001	0.00005	0.00002	0.000023
Potassium (K ⁺)	0.793	1.133	0.59	0.83867	0.274365
Sodium (Na ⁺)	19.34	27.64	10.5	19.16000	8.571418
Sulphates (SO ₄ ²⁻)	1.649	4.309	9.37	5.10933	3.922226
Lithium (Li ⁺)	0.00043	0.0013	0.002	0.00124	0.000787
Rubidium (Rb ⁺)	0.000234	0.000259	0.000532	0.00034	0.000165
Bromides (Br ⁻)	0.164	0.201	0.05	0.13833	0.078704
Scandium (Sc ³⁺)	0.00001	0.00001	0.000017	0.00001	0.00004
Vanadium (V ³⁺)	0.0001	0.0001	0.000725	0.00031	0.000361
Gallium (Ga ³⁺)	0.000579	0.002	0.0002	0.00093	0.000949
Indian (In ³⁺)	0	0.00001	0.00001	0.00001	0.00006
Molybdenum (Mo ⁴⁺)	0.0001	0.0001	0.000017	0.00007	0.000048

Table 3Concentration of the selected elements contained in the rejection from desalination plants per unit volume (kg/m³). Source: own elaboration.

Elements	Atlantic Ocean	Mediterranean Sea		Brackish groundwater			
Concentration	Single value	Minimum	Average	Maximum	Minimum	Average	Maximum
Boron (B)	0.006647	0.006086	0.007504	0.00892	0.002004	0.003397	0.00479
Calcium (Ca ²⁺)	0.717000	0.713000	0.769500	0.82600	1.311000	1.432500	1.55400
Strontium (Sr ²⁺)	0.014000	0.014000	0.020000	0.02600	0.028000	0.034000	0.04000
Magnesium (Mg ²⁺)	2.143000	2.070000	2.170500	2.27100	0.590000	1.085000	1.58000
Sodium (Na ⁺)	19.340000	15.890000	21.765000	27.64000	1.968000	6.234000	10.50000
Lithium (Li ⁺)	0.000430	0.000440	0.000870	0.00130	0.001500	0.001750	0.00200
Rubidium (Rb+)	0.000234	0.000233	0.000246	0.00026	0.000035	0.000284	0.00053
Gallium (Ga ³⁺)	0.000579	0.000200	0.001100	0.00200	0.000200	0.000200	0.00020
pH	7.8	7.4	7.7	8.1	7.5	7.55	7.6

considered reasonable due to losses caused by crystallisation or precipitation forms of the different elements and materials. We will consider a recovery level of 60 % as a probable value to determine the economic valuation of the extraction system due to the diverse nature of desalination brines and based on different recovery techniques [17].

2.2. Market prices

Part of the element selection strategy is based on their economic value. There is a huge potential for the commercial application of the elements listed above. Some of them, due to their relative scarcity [38], have very high market prices. The price of these elements, like any commodity, is subject to the laws of supply and demand. International markets for these products are highly volatile and have very wide price ranges depending on many factors (economic situation, concentration of supply or demand, geopolitical context, existence of conflicts, etc.).

The international prices for these elements (Table 4) have been obtained from spot markets in the final months of 2022. The main industrial markets are in China. Therefore the prices of these elements have been obtained in Chinese currency (renminbi — CNY) with an exchange rate or conversion to the euro fixed at a rate of 7.42 CNY per euro (28/

12/2022). We have attempted to locate several sources to obtain different price ranges for each element and determine values between two levels (minimum and maximum) in order to contemplate several possibilities.

From these price ranges, applied to the different elements and their quantities found in the different analyses of the reject waters, we can determine the potential economic value of commercially exploiting these elements, according to the type of installation (capacity), its location and the type of resource it uses.

At the research stage, the economic analysis needs to evaluate the potential revenue derived from selling the recovered elements, taking into account the current market prices and the expected demand for the elements. This step can help determine the feasibility of recovering some elements and materials from the rejected brine of the desalination plants.

3. Results

3.1. Value per cubic metre

From the above data on the composition and the different elements

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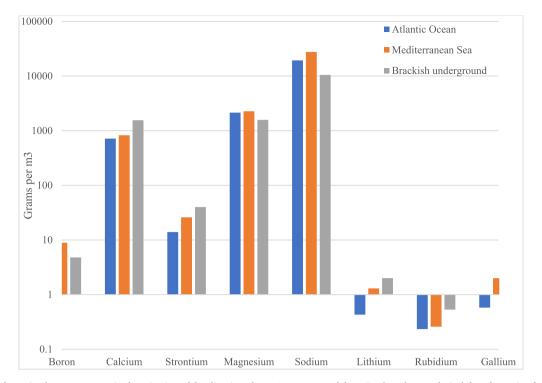


Fig. 1. Quantity of certain elements present in the rejection of desalination plants. Source: own elaboration based on analytical data from nine facilities in different locations. Samples taken in September 2022. Figures in grams per cubic metre (g/m^3) . Data in logarithmic scale.

Table 4 International wholesale prices of different elements. Source: own elaboration based on data contained in various sources of international wholesale markets. Figures in euros per kilogram (ℓ /kg). Date consulted: 28/12/2022.

Elements	Price €/kg (28/12/2022)		
	Lowest	Highest	
Boron	0.75	0.94	
Calcium	0.43	1.89	
Strontium	9.91	56.60	
Magnesium	3.08	3.08	
Sodium	0.67	2.02	
Lithium	382.75	411.05	
Rubidium	9433.96	12,129.38	
Gallium	1698.11	1745.28	

present in the reject water from desalination facilities, we can obtain a value for each unit volume of this reject water by adding up the different international prices obtained for each of the elements. If we could extract and separate all the elements analysed in their totality, we could obtain around 100 euros/unit volume ($\rm m^3$). However, as mentioned above, in addition to the fact that it is not possible to extract 100 % of the quantity of each element present, some of them are found in low quantities or their price is not high enough to be considered for large-scale commercial exploitation.

The commodities market has behaved in a very volatile way in recent years [39,40]. Many elements have multiplied their price by up to 20 times in the last five years, causing a major impact on the industrial sector and triggering a global mining fever. The price of elements in high demand for today's industrial activities, such as lithium (Li) or rubidium (Rb), have soared in the last three years as a result of these market

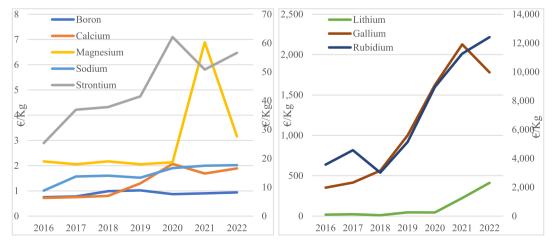


Fig. 2. Evolution of international prices of some raw materials. Source: own elaboration based on information from market operators. Figures in euros/kg. Data in logarithmic scale. On the left side, strontium corresponds to the right axis, while the others correspond to the left axis. On the right side, rubidium corresponds to the right axis and lithium and gallium to the left axis. This has been done to show more clearly the recent trend in the prices of the eight selected elements.

circumstances. Looking ahead, in the short to medium term, volatility looks set to continue due to the relative scarcity of these elements. As we can see in Fig. 2, the price evolution shows an upward trend. The rising prices for these products clearly show the existence of a market for the elements that can be extracted from the salt concentrate produced during desalination. The recovery of this concentrate would increase the supply of raw materials, thereby reducing their relative scarcity.

The selection of the eight elements has been made considering the market conditions and the potential volume that could be extracted from the brine. Taking into account the composition of this rejection depending on the location and the type of resource used, the economic valuation that can be obtained from each cubic metre of these installations is presented in Table 5 and ranges from 39 to 72 euros.

Within this range of amounts, it is worth highlighting the importance of sodium (Na), which can represent between 54 % and 77 % of the total estimated amount per unit volume, with a value between 21 and 56 euros/ $\rm m^3$ of waste. Without this element, the value corresponding to the sum of the remaining seven elements would be in the range of 13–18 euros/ $\rm m^3$ of reject water.

Due to the different composition of the reject waters depending on their uptake, the most valuable elements differ between brines from different facilities. Facilities using brackish underground resources have economic potential in elements such as calcium (Ca), lithium (Li), rubidium (Rb) and strontium (Sr). These four elements have a combined total value of more than $12 \, {\rm euros/m^3}$ of rejected brackish groundwater.

Installations using seawater as a resource source have three components in sufficient concentrations and high price levels with a combined value of between 10 and 13 euros/m³ of rejection. These elements are magnesium (Mg), rubidium (Rb) and gallium (Ga).

3.2. Production and revenue potential

In the selection of the elements that could be recovered, as indicated in the methodology section, we will consider a recovery potential on an industrial scale of 60 % of the elements. This level of efficiency is a consequence of factors that are complex to control, such as possible losses, the efficiency of the processes, the mechanisms of crystallisation or precipitation of the salts, etc.

Another element to consider is the size of the facilities. The current facilities and the maximum design capacity of the plants determine desalinated water production capacities of around 55,000–330,000 m³/day, which implies a level of rejections of around 20–120 hm³/year.

Plants using brackish groundwater have a limitation of available resources and are smaller in size and capacity, in the range of $30,000-60,000\ m^3/day$. However, seawater plants do not have these limitations and can have a higher processing capacity.

Applying the prices of the different elements to the production capacities, with an estimated recovery potential of 60 %, in the case of installations processing brackish groundwater with a maximum capacity of about 20 hm³/year, we have calculated an annual revenue potential

Table 5 Valuation of the different elements contained in the rejection from desalination plants per unit volume (m). Source: own elaboration based on analytical data and market prices of the different elements. Figures in euros per cubic metre (ϵ/m^3) .

-			
Elements	Atlantic Ocean	Mediterranean Sea	Brackish groundwater
Boron	0.0063	0.0084	0.0045
Calcium	1.3528	0.4208	2.9321
Strontium	0.7925	1.4717	2.2642
Magnesium	6.5994	6.9936	4.8656
Sodium	39.0970	55.8760	21.2264
Lithium	0.1768	0.5344	0.8221
Rubidium	2.8383	3.1415	6.4528
Gallium	1.0105	3.4906	0.3491
Total	51.8735	71.5246	38.9168

of between 230 and 467 million euros, as shown in Table 6.

Two thirds of the revenues come from just two elements: magnesium (Mg) and sodium (Na). Taking into account all other elements and materials, the recovery of a few tonnes of lithium (Li), rubidium (Rb) and strontium (Sr) has a potential value of almost 74–115 million euros/year. The total weight of these three elements is less than 31 tonnes/year after processing a total of 20 million tonnes of reject water. In addition to these elements, boron (B), calcium (Ca) and gallium (Ga) would have an additional economic contribution of another 15 million euros/year. This amount is much higher than the cost of desalination applied to the production of new water resources, which is the main function of the facility.

Plants using marine sourced resources can incur higher processing capacities with almost unlimited resources. The only constraint would be the technology and availability of land for the facilities, as well as energy resources.

The average capacity of the facilities located in Spain is around $220,000 \, \mathrm{m}^3/\mathrm{day}$ of desalinated water production, around $80 \, \mathrm{hm}^3/\mathrm{year}$. For this level of treatment, the revenue potential is much higher than for facilities using brackish groundwater resources, in fact, up to almost eight times more.

Installations using marine resources from the Atlantic Ocean, considering their composition and with an efficiency of 60 % in the extraction of the elements and materials contained in the plants' reject waters, have a revenue potential in the range of 1125–2490 million euros/year. In the case of installations using brackish water, 87.5 % of this potential income (some 942–2143 million euros/year) comes from sodium (Na) and magnesium (Mg), with an annual extraction of more than 1.03 million tonnes of these elements.

Considering only the contributions of three elements, some 672 tonnes/year of strontium (Sr), 11.2 tonnes/year of rubidium (Rb) and 27.8 tonnes/year of gallium (Ga) could be extracted. Potential revenues from the extraction of these three elements would be in the order of 160-223 million euros/year.

Finally, the results of the facilities located in the Spanish Mediterranean are presented. They have similar water processing capacities to those located in the Atlantic Ocean, but with slight variations in their composition.

These facilities have a revenue potential ranging from around 1564 million euros at the lower price level of the different elements to 3507 million euros at the upper price level of the price range of the different materials. However, as in the other two cases, slightly more than 85 % of these revenues come from the two most abundant elements considered, magnesium (Mg) and sodium (Na).

In the case of these installations, there are three elements that provide a large source of income, although they are not very abundant in the reject concentrate of desalination facilities. Some 1248 tonnes/year of strontium (Sr), 12.4 tonnes/year of rubidium (Rb) and 96 tonnes/year of gallium (Ga) could be extracted, with potential revenues of between 293 million euros and 389 million euros/year.

If we take into account the current existing desalination capacity in Spain, with almost 100 large-scale facilities, with a production volume of more than $10,000 \, \text{m}^3/\text{day}$ [41], up to almost $800 \, \text{hm}^3/\text{year}$ of rejected water from the facilities could be used with an economic potential capable of generating, at most, between $13.4 \, \text{and} \, 29.8 \, \text{billion}$ euros/year in revenue.

Up to 548 t of lithium (Li), 143 t of rubidium (Rb), 655 t of gallium (Ga), 12,246 t of strontium (Sr), 3668 t of boron (B), 440,752 t of calcium (Ca), 1.01 million tonnes of magnesium (Mg) and 10.88 million tonnes of sodium (Na) could be extracted. The revenue potential of the first four elements in this list alone would represent an annual revenue potential of around 3.8 billion euros, accounting for 13 % of the total potential revenue, despite representing only 0.1 % of the volume of elements considered.

Table 6
Production potential and economic value of the elements recovered from rejects in desalination installations. Source: own elaboration based on analytical data and market prices of the different elements. Capacity and potential figures in kilograms and value in euros. Calculations based on a plant with a production capacity of around 55,000 m³/day or 20 hm³/year for brackish underground resources and of around 220,000 m³/day or 80 hm³/year for marine water.

	Elements	Elements Total capacity (kg/year) Potential kg/year (6		Value (€)	e (€)	
				Lowest	Highest	
Brackish underground resources	Boron	95.8	57.48	43,381	54,226	
	Calcium	31,080,000	18,648,000	8,092,528	35,184,906	
	Strontium	800	480	4,754,717	27,169,811	
	Magnesium	31,600,000	18,960,000	58,387,601	58,387,601	
	Sodium	210,000,000	126,000,000	84,905,660	254,716,981	
	Lithium	40	24	9,185,984	9,865,229	
	Rubidium	10.64	6384	60,226,415	77,433,962	
	Gallium	4	2.4	4,075,472	4,188,679	
	Total	273,630,440	164,178,264	229,671,758	467,001,396	
Atlantic Ocean	Boron	531.76	319,056	240,797	300,996	
	Calcium	57,360,000	34,416,000	14,935,245	64,935,849	
	Strontium	1,120,000	672	6,656,604	38,037,736	
	Magnesium	171,440,000	102,864,000	316,771,213	316,771,213	
	Sodium	1,547,200,000	928,320,000	625,552,561	1,876,657,682	
	Lithium	34.4	20.64	7,899,946	8,484,097	
	Rubidium	18.72	11,232	105,962,264	136,237,197	
	Gallium	46.32	27,792	47,193,962	48,504,906	
	Total	1,777,751,200	1,066,650,720	1125,212,592	2,489,929,675	
Mediterranean Sea	Boron	713.68	428,208	323,176	403,97	
	Calcium	66,080,000	39,648,000	17,205,736	74,807,547	
	Strontium	2,080,000	1248,000	12,362,264	70,641,509	
	Magnesium	181,680,000	109,008,000	335,691,752	335,691,752	
	Sodium	2,211,200,000	1,326,720,000	894,016,173	2,682,048,518	
	Lithium	104	62.4	23,883,558	25,649,596	
	Rubidium	20.72	12,432	117,283,019	150,792,453	
	Gallium	160	96	163,018,868	167,547,170	
	Total	2,462,038,400	1,477,223,040	1,563,784,545	3507,582,514	

4. Discussion

The results obtained in this article are novel, as such an assessment has never been carried out before. Many studies have found that the extraction of valuable elements from salt concentrate would reduce pollution from effluent while providing economic value [2,17,26,31]. However, the analyses have been restricted to the laboratory scale [16]. The assessment made in this study, reflecting various Spanish desalination plant analytics, provides useful revenue potential for the evaluation of brine mining strategies and is a good reference for the potential of this mining activity.

The technical aspect has received increasing attention in recent years, with the assessment of various technologies and elements [5,17,25], but it is currently only a proposal which is being analysed at laboratory scale, with economic analyses taking a back seat. The technical studies carried out address the extraction of elements both individually, as in the cases of Naidu et al. [42] for rubidium or Khalil et al. [29] and Xiong et al. [43] for lithium, and jointly, with cases such as Bunani et al. [18] for boron and lithium, Zhang et al. [44] for magnesium and lithium or Nieto et al. [45] for magnesium, lithium and calcium. In these technical studies, the economic part is either absent or reduced to basic questions such as the cost of extraction or the market price of the extracted product. In other words, a series of investigations are being carried out on technical issues without knowing the economic value that would be obtained from their application.

Economic viability is essential and is made up of several factors as indicated by Ortiz-Albo et al. [15], who did consider economic aspects such as the market trend, the risk associated with the product, its possible application and the price and profitability obtained, but without studying in more detail the value contained in the salt concentrate that is currently discharged into the environment. These factors are related to the revenue potential of the different extractable elements and, together with the extraction costs, can determine the economic viability of this mining activity [17,31,46]. This article focuses on calculating the value contained in the salt concentrate

produced during the desalination process and making a selection of elements with the highest potential for revenue generation. Each element has a specific utility and market, and while there are differences in terms of demand and market opportunities between elements [36], the existence of a market price for all of them is an indication that there is a potential demand for the extracted materials.

The key aspect of the analysis is the selection of the elements with the highest revenue potential within the salt concentrate. This is a little-studied issue, as the analyses focus on the technical aspect and extraction costs, but there are previous studies such as those by Ortiz-Albo et al. [15], Loganathan et al. [25] and Shahmansouri et al. [36] that have examined the economic aspect of this mining activity.

These works present major differences in the selection of elements, differences which also arise if we compare the results of this analysis with those of these three previous articles. This highlights the importance of analysing the composition of the salt concentrate and the value of the elements present in it before making a decision on the extraction technology to be used. A quick comparison of the element selections of these papers shows that Ortiz-Albo et al. [15] associate the recovery of boron with a high risk, which is reasonable given that it is neither particularly abundant nor has a high price, Loganathan et al. [25] find it economically viable and Shahmansouri et al. [36] do not include it in their selection of elements. Another case of note is that of gallium, as these three studies do not find its recovery viable, while the data in this article show that its high price makes its scarce presence in salt concentrate valuable. The reverse situation occurs with bromine, as its price of around €4/kg is insufficient to compensate for the small amount extractable, but the previous element selections make it economically viable. There are also points in common between these references and our findings, such as the high value of rubidium, which is scarce in the salt concentrate but has a high price, and that of magnesium and sodium, which do not have a high price but the large extractable quantity makes them potential sources of revenue.

The analysis was based on the quantities and prices of the elements present in the salt concentrate produced by desalination plants from three different sources. This is something significant that would affect the element recovery project, highlighting differences between brackish and marine waters, with the former having a higher quantity of calcium, lithium and rubidium and a lower quantity of sodium and gallium. Of the two types of marine waters, those of the Mediterranean Sea stand out for the higher presence of the eight elements included in the analysis compared to the waters of the Atlantic Ocean. This fact reinforces the aforementioned need for an economic assessment such as the one in this article. Although there are general criteria that can be followed, the variability of prices and the composition of water according to its origin are key elements that make it necessary to continuously update the analysis of brine mining. These two fundamental variables are related to the optimal techniques for the extraction and recovery of these materials. Among others, this would be the case, for example, of lithium carbonate (Li₂CO₃). Given the presence of both elements in the reject concentrate, it is possible to assume its extraction by precipitation in this form. Their direct application in the electronics or chemical industries, as well as in battery components, suggests that these salts are suitable for commercial exploitation.

5. Conclusions

This study conducts a first approach to determining the economic potential of mining salt concentrate from reject brine water coming from desalination plants. The concentration of certain elements for which there is a strong demand due to their present industrial applications has led to a sharp rise in the prices of these elements in recent years.

The markets are subject to strong volatility indicating a continuous and sustained upward trend in certain elements available in the saline reject concentrates from desalination plants. This behaviour makes the estimation of a future value for these materials unpredictable but allows us to foresee a growing income potential.

Considering the results of the study, the economic value of the extracted elements from the reject flows of desalination facilities in Spain – having selected boron, calcium, strontium, magnesium, sodium, lithium, rubidium, and gallium – could reach between 13.4 and 29.8 billion euros/year. Taking into account only the most valuable elements, which account for only 0.1 % of the total volume, the potential revenue would amount to around 3.8 billion euros/year. The remaining elements, although less valuable, have potential due to their concentration in the salt rejects. Thus, the high presence of sodium in the reject water, whose price ranges from $\{0.67/kg\ to\ \{2.02/kg\ shows\ the\ highest\ revenue\ potential\ of\ the\ eight\ selected\ elements.$

One of the main conclusions reached in this article is the optimisation of the selection of recoverable elements in the salt concentrate. This has been done based on analysing desalination plants in Spain and international prices of the elements present in these samples, considering both the concentration and the trends in commodities markets in two significant locations of Spain in terms of desalination capacity: the Atlantic Ocean and the Mediterranean Sea. The results obtained enable to focus on the elements with the highest revenue potential, thus facilitating the design of the recovery process focused on the most profitable ones. The result is a range of potential revenues that could be integrated into a comprehensive analysis, which would include the associated costs to extract elements, as well as transport and marketing expenditure. Cost analysis is another key factor in determining the viability of brine mining and, in order to finally determine the feasibility of this mining activity, it will also be necessary to study the market for these elements because, although the price already indicates that a market exists, where it is located should also be taken into account. Further analysis should be conducted along these lines. Nevertheless, if we know what the value of the extracted elements is, according to commodity pricing, it will help us to estimate what we are willing to pay by investing in feasible extraction technologies, to obtain benefits from integral operational strategies for recovering desalination reject concentrates.

In addition to the economic potential of these resources, there are

further benefits to be gained from additional advantages, such as the elimination or reduction of salt concentrate discharges, savings in transport and the transaction costs of raw materials, as well as the considerable reduction in environmental damage caused by traditional mining, which would be studied in future research approaches by integrating the financial analysis into a holistic cost-benefit assessment, taking into account the overall performance of a particular project, including the benefits for society as a whole.

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CRediT authorship contribution statement

Alberto del Villar: Conceptualization, Data curation, Formal analysis, Funding acquisition, Methodology, Writing – original draft. Joaquín Melgarejo: Conceptualization, Funding acquisition, Project administration, Writing – review & editing. Marcos García-López: Conceptualization, Data curation, Funding acquisition, Investigation, Writing – review & editing. Patricia Fernández-Aracil: Conceptualization, Formal analysis, Funding acquisition, Investigation, Writing – original draft, Writing – review & editing. Borja Montano: Conceptualization, Funding acquisition, Project administration, Writing – review & editing.

Declaration of competing interest

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

Data availability

The information used on the elements present in the salt concentrate produced during desalination has been provided by a company in the sector on a confidential basis. This information is therefore not published in any repository and it is not possible to give a greater level of detail on the plants whose rejection was analysed. The other key element of the analysis is the market prices of the elements present in the concentrate, which are provided by the main market operators. The prices for boron, calcium, strontium and gallium are from the Made-in-China website (https://www.made-in-china.com/), sodium, lithium and rubidium prices are from the SMM website (https://www.metal.com/) and that of magnesium comes from TradingEconomics (https://es.tradingeconomics.com/).

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