



Geothermal Water Desalination in Greece's Islands, Coupled with Extracting Precious Metal Salts from the RO Retentate [†]

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Abstract

Many Greek islands host geothermal springs whose waters can be desalinated to produce drinking water. Some of these waters contain meaningful concentrations of the valuable Rb⁺ and Cs⁺ ions, which, when extracted from the desalination brine as RbCl and CsCl salts, can yield revenues exceeding the freshwater production costs. We demonstrate the use of reverse osmosis (RO) to produce freshwater and apply theoretical simulations to assess a proven extraction method applied to the RO retentate of geothermal water from Samothrace, characterized by [Rb⁺] = 2.72, [Cs⁺] = 0.55, [K⁺] = 514, [Na⁺] = 3759 (all in mg/L) and pH 6. The extraction method, developed by the authors, relies on ion exchange using a PES-coated Zn-hexacyanoferrate sorbent with high affinity for monovalent cations (no affinity for multi-valent cations), followed by a unique ion-chromatography separation. We show that the production cost remains <25% of the salts' market price, with ROI of ~4.5 years.

Keywords: rubidium; cesium; geothermal waters; Greek islands; Zn-HCF; resource recovery

1. Introduction

Water scarcity is emerging as a pressing challenge across the Greek islands. A complex interplay of climate change, unsustainable tourism, migration fluctuations, aging water infrastructure, and uncoordinated policy responses has left many islands vulnerable to drought and water insecurity [1,2]. Beyond the physical absence of freshwater, particularly during the tourism season, the crisis also reflects deeper governance failures; i.e., fragmented responsibility between municipalities, regional authorities, and national agencies has led to a patchwork of reactive measures rather than systemic planning. Meanwhile, the accelerating pace of climate change, as observed by the European Environment Agency (EEA), intensifies seasonal imbalances and exacerbates long-standing inequalities between islands with natural aquifers and those dependent on rainfall or transfers [3].

Data from the EEA confirm that Greece's freshwater abstraction index has exceeded sustainable thresholds in several regions, placing it among the EU countries with the highest relative natural resource water exploitation. This is especially problematic in the islands' context, where inter-annual variability is high, and aquifer recharge is limited [3]. Additionally, the World Bank (2021) has drawn attention to the role of water scarcity as



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a driver of migration and social destabilization. In small, exposed communities, such as those on remote islands, the inability to ensure water security may drive both outward migration and inter-community tension, particularly when coupled with refugee influxes or economic instability [4].

Seawater desalination requires massive infrastructure investment and a large energy input that is limited in most Greek islands. However, desalination of brackish water involves lower investment and energy consumption. Many of the Greek islands, including Samothrace, have extensive brackish groundwater networks that are unsuitable for drinking or irrigation but could serve as an alternative source for desalination. Mature, commercially available technologies now exist for desalinating brackish water. While effective, desalination requires energy and financial investment to produce two outputs: clean, potable water and a concentrated brine byproduct (termed “retentate”). Such operation presents three major challenges: obtaining the highest possible recovery ratio (i.e., the volume of freshwater that is produced relative to the volume of the source saline water), an environmental solution to the disposal of the retentate, and the financing of the construction and operation of the desalination facility.

Geothermal springs generate substantial volumes of hot aqueous solutions rich in dissolved minerals, including rare earth elements (REEs), Li^+ , Rb^+ , Cs^+ and Mn^{2+} . These metal-ion-rich solutions, once considered waste, are now recognized as valuable mineral sources, offering potential synergies between energy production and critical metal extraction [5–7]. Unlike traditional mining, extraction from geothermal brines involves fewer steps and produces less solid waste, making it a promising green mining alternative.

Until recently, most of the focus has been on extracting Li^+ , but geothermal brines contain other valuable alkali metal ions, such as rubidium and cesium, although typically at lower concentrations [8]. These metal ions share similar extraction challenges due to their low concentrations and the presence of competing monovalent cations (e.g., Na^+ , K^+), but also a much higher market value per unit mass. Biological recovery techniques such as biosorption and bioaccumulation have been proposed as environmentally friendly alternatives, particularly suited for low-concentration recovery scenarios [9]. However, physicochemical methods, including ion exchange or selective electrodialysis, offer higher selectivity and scalability for Rb^+/Cs^+ separation from geothermal matrices.

The geothermal waters of the island of Samothrace are mineral-rich, containing a range of critical and strategic materials, including rare ions such as Rb^+ and Cs^+ [10]. The market potential for rubidium salts is rapidly growing, driven by its essential role in advanced technologies and industrial applications [11,12]. Rb^+ salts are high-value compounds used in the production of fiber optics, atomic clocks, biomedical research, and aerospace systems [13]. Similarly, Cs^+ salts are used in oil and gas exploration, energy conversion devices, and chemical catalysis [14–16]. Both rubidium and cesium salts are classified as minerals of interest by the US government as they appear in the “Critical Mineral List, 2025” published by the USGS. Geothermal brines, therefore, represent a promising alternative source for securing sustainable and economically viable supplies of these strategic elements [17]. This paper offers a dual-impact solution to two emerging security threats: climate-induced water scarcity and strategic dependence on critical minerals. By applying a chromatographic selective separation process as described by [18,19] on a reverse osmosis (RO) desalination plant brine, based on a Samothrace geothermal water sample, it may simultaneously provide freshwater and enable local extraction of rubidium and cesium salts, whose revenue is expected to exceed the production costs of both desalination and salt extraction plants. Such a solution has high benefits for the islanders, including increased water supply security and higher water allocation for tourism and agriculture, all of which result in improved social stability.

2. Materials and Methods

2.1. Samothrace Geothermal Water Source

According to [10], the island of Samothrace, Greece, contains several geothermal brine sources, the full composition of which appears in [10]. This work focused on three sources (A Pigi 1 and 2, and B Pigi) using the average of all three sources, with the alkali metal conc.: Na = 3759, K = 541, Cs = 0.55 and Rb = 2.72 mg/L (temperature 48–51.5 °C, pH 6.1–6.6, TDS 11,079–13,801 mg/L). We chose to work on this water because of its relatively high Rb⁺ and Cs⁺ concentrations; however, many other geothermal waters in the Greek islands may be appropriate for the operation described herein.

2.2. Full Process Simulations

For the simulation, the PHREEQC software (Ver. 3.8.6.17100) [20] was used with the wateq4f.dat database. The following data of the ion exchange separation factors for Zn-hexacyanoferrate (Zn-HCF) (Li⁺, Na⁺, K⁺, NH₄⁺, Rb⁺, and Cs⁺ of $\alpha_{Na}^i = 0.4, 1, 49, 101, 315, 3790$, respectively [18,21]) were used with the EXCHANGE and ADVECTION reactions.

PHREEQC was used to simulate chromatographic-based separation of RbCl_(s) and CsCl_(s) based on a previously proven concept [18,19]. According to this method, a three-stage chromatographic desorption sequence was used to recover the adsorbed monovalent cations (K⁺, Na⁺, Cs⁺, and Rb⁺) onto Zn-HCF PES resin. The first desorption step employed a low-concentration NH₄Cl eluent (0.05 M), followed by a second step using a high-concentration eluent (1 M) for recovering Rb⁺, followed by applying a very high-concentration NH₄Cl eluent (3 M) for extracting Cs⁺. Subsequent sublimation and condensation enabled the separation and recycling of NH₄Cl from RbCl and CsCl, producing highly pure RbCl and CsCl salts (>99%). Table 1 depicts the various stages of the ion exchange process.

Table 1. Schematic representation of the process stages. *Following the regeneration with NH₄⁺, and prior to the next adsorption step, the 1st column is regenerated with NaCl, to replace the NH₄⁺ with Na⁺.

#	Column	Pre-Loaded Cation	Adsorption Solution	Regeneration Solution	Main Goal
1	1st	Na ⁺	RO retentate of the Pigi geothermal water	4.0 M NH ₄ Cl	Adsorption of Rb ⁺ and Cs ⁺
2	1st IC	NH ₄ ⁺	1 M salt mixture, following NH ₄ Cl removal	0.05 M NH ₄ Cl	Removal of K ⁺ , Na ⁺
				1.0 M NH ₄ Cl	Selective separation of Rb ⁺
3	2nd IC	NH ₄ ⁺	The outlet of 1st IC column regeneration step with 0.05 M	3.0 M NH ₄ Cl	Selective separation of Cs ⁺

3. Results and Discussion

3.1. Desalination as an Initial Step, Including Silica Removal

Using the chemical composition data [10] of the chosen three sources, their respective osmotic pressures (OPs) were calculated using the PHREEQC software with the Pitzer database [20]. Because seawater RO desalination is limited by a final brine OP of approximately 50 bars, this value was set as the maximum threshold. A Pigi initial OP of 10 bar was calculated and selected for estimating the RO recovery ratio (RR), with a concentration factor of 5 (80% RR). Typical brackish water RO limitations on the RR include precipitation of gypsum and silica solids [22–24]. The gypsum saturation index (SI) was below the recommended

value ($SI = 0.4$) of the antiscalant (AS) manufacturer when RR of 80% was applied. The silica concentration is, however, limiting. An initial silica concentration of 74 mg/L enables an RR of 67% without treatment, as the maximal silica concentration recommended by AS manufacturers is 200 mg/L [22]. This limitation can be overcome by applying pretreatment to the feed or brine to remove excess silica, as demonstrated in [22,25,26].

3.2. First and Second Adsorption Steps

Zn-HCF has specific (low and medium) affinities for Na^+ and K^+ , and high affinities for Rb^+ and Cs^+ . It does not adsorb divalent ions, nor does it adsorb Li^+ . As a result, due to the lower concentration of Rb^+ and Cs^+ compared to K^+ and Na^+ , a relatively high solution volume is needed to reach equilibrium with respect to Rb^+ (the main ion target, due to its very high cost and relative ease of extraction). The breakthrough curve based on the RO brine of the Samothrace geothermal water is shown in Figure 1A. As appears in Figure 1A, the adsorbed Rb^+ reaches a plateau at 120 bed volumes (BV). To reach an optimum Rb/Cs ratio and as low as possible Rb^+ loss, the first adsorption stage should be terminated past 75 BV (vertical dashed line). At this stage, i.e., end of the first adsorption stage, Rb^+ filled 1.28% of the adsorption sites, while Cs^+ filled 0.17% of the sites (molar-based). Assuming that the adsorption step is stopped after 75 BV, the Rb^+ adsorption efficiency would be 94.6%.

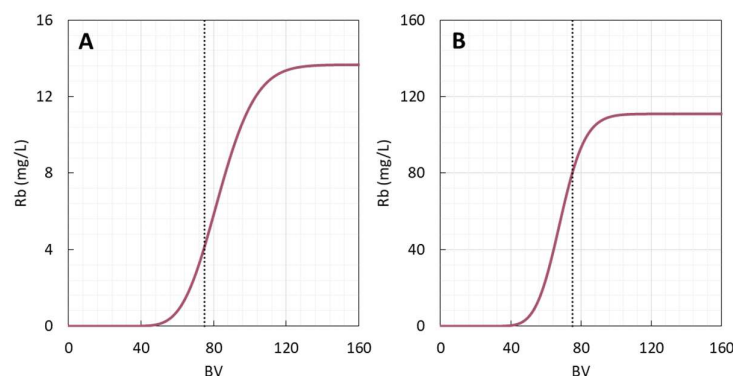


Figure 1. Breakthrough curve for (A) first adsorption stage; (B) second adsorption stage.

Following the first adsorption stage, full regeneration with 4 M NH_4Cl needs to be performed to desorb all the cations from the column and replace them with NH_4^+ . The NH_4Cl is then removed and recycled via sublimation/deposition, following which a mixture of KCl, NaCl, RbCl, and CsCl solid salts remains. Each mole of mixed salts obtained from the regeneration–sublimation of the first stage is then dissolved in 10 L of distilled water. The obtained brine, with Rb^+ and Cs^+ concentrations of 109.1 mg/L and 23.1 mg/L, respectively, is then fed to a second Zn-HCF adsorption column (1st IC, Table 1). The simulation of the second breakthrough curve appears in Figure 1B. The step is terminated after 70 BV, at which point the column is loaded with 9.14% Rb^+ and 1.37% Cs^+ , respectively. Rb^+ and Cs^+ adsorption efficiency in this step were 92.36% and 99.94%.

3.3. Simulation of the Chromatographic Desorption Steps

To perform the chromatographic desorption, a second Zn-HCF column (2nd IC, Table 1), pre-adsorbed with NH_4^+ , was assumed to be placed in series, downstream of the first, loaded column. The size of the second IC column equaled the first IC. The chromatographic desorption stage consists of two sequential steps: (1) Na^+ and K^+ desorption via the passage of a low eluent concentration (0.05 M NH_4Cl), as shown in Figure 2A; (2) Rb^+ and Cs^+ desorption via higher eluent concentration (1 and 3 M NH_4Cl) as in Figure 2B.

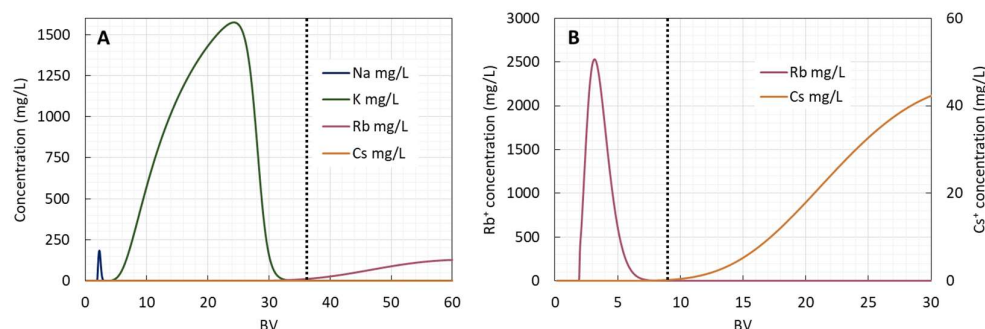


Figure 2. Chromatographic-based separation with NH_4Cl as the eluent. (A) First stage with 0.05 M eluent for Na^+ and K^+ removal. (B) Second stage using 1 and 3 M NH_4Cl for Rb^+ and Cs^+ separation, respectively (note that the 3 M Cs^+ separation simulation is not shown, for lack of space).

According to the simulation, after ~ 36 BV, the Na^+ and K^+ concentrations at the exit of the column drop to zero. At this point, the eluent concentration can be increased to 1 molar. This means that after ~ 36 BV, no Na^+ and K^+ are adsorbed on either column. In contrast, the Rb^+ remains almost entirely adsorbed but largely moves towards the second column. The Cs^+ , in contrast, remains mostly adsorbed on the first column.

Subsequently, operation at elevated eluent concentration (1 molar) for 9 BV, resulting in the release of most of the adsorbed Rb^+ . From BV 9–10, the solution comprises high Rb^+ concentrations and low Cs^+ concentrations. This stream can now be recycled backwards to an earlier stage of the process. After that point, all the Rb^+ is released, and the eluent concentration can be increased to 3 M to release the Cs^+ mass sharply and rapidly (graph not shown).

3.4. Plant Description and Cost Assessment

Based on the proposed Rb/Cs separation from the desalination retentate stream ($5 \text{ m}^3/\text{h}$), three Zn-HCF columns, 2750 L each, are planned in the first Rb/Cs extraction stage, and three 188 L Zn-HCF columns for the second chromatographic and Rb/Cs purification. Both stages also include mechanical vapor recompression/salt drying/ammonium chloride sublimation systems and storage tanks, supporting the Rb/Cs extraction operation. The forecasted RbCl -Rb and CsCl -Cs extracted mass will be 518 and 375 kg/y, respectively. The plant's capital investment was estimated at M\$14.9. The gross annual profit (income minus annual costs) is M\$3.59. The resultant project ROI is 4.16 years, assuming 4.99% interest rate (average 2025 in Greece) and plant life of 25 years. A detailed breakdown of the costs is available from the authors upon request.

4. Conclusions

PHREEQC simulations that are based on empirically determined selectivity coefficients have been shown in [18,19] to provide reasonably accurate predictions. Here we simulated treatment of geothermal water from Samothrace to assess the feasibility of desalinating the water and then extracting pure $\text{RbCl}_{(s)}$ and $\text{CsCl}_{(s)}$ from the RO retentate via a proven chromatographic separation process. This integrated approach offers dual benefits: it ensures a reliable and cost-effective supply of high-quality water for the island's residents while simultaneously recovering valuable salts through resource recovery from the RO waste stream. Cost assessment of the metal recovery step (flow rate of $5 \text{ m}^3/\text{h}$) revealed very high cost-effectiveness, with a predicted ROI of ~ 4.5 years for both the desalination and the mineral extraction plants. The authors acknowledge that social acceptance may be challenging in these types of projects. We emphasize that the primary objective of the project is water security for the local communities, while resource recovery is performed to support economic viability. Transparency, communication, and tangible

local benefits (secure water supply, enhancement of local employment) are the main keys to implementation.

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