

Mineral Extraction from Geothermal Reservoirs: A Case Study from Western Anatolia

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ABSTRACT

Geothermal brine is a promising source for sustainable and environmentally friendly mineral extraction, containing a variety of valuable minerals, such as silica, lithium, strontium, and rare earth elements. However, the low mineral concentrations in the brine present a significant challenge, requiring large volumes of brine to be processed. This study investigates the potential of mineral extraction from geothermal reservoirs, using a case study of reserve estimation in a geothermal field to demonstrate the application of Monte Carlo simulation, a stochastic approach used to handle uncertain parameters with critical effects on reserve estimation. A review and evaluation of mineral extraction methods is then presented, highlighting their challenges, advantages, and techno-economic perspectives. The study found that mineral extraction from geothermal reservoirs is economically viable, although more research and development is needed to overcome the challenges associated with this process.

1. INTRODUCTION

Diverse technological solutions, encompassing membrane separation, ion exchange, precipitation, biosorption, and adsorption, is currently under development for the extraction of valuable minerals from geothermal brines (Table 1). Each methodology offers distinct advantages and faces specific challenges, prompting ongoing research efforts dedicated to process optimization. Recognizing the substantial potential of these resources, several regions boasting significant geothermal reserves have initiated pilot projects and demonstrations. These initiatives aim to gauge the feasibility of large-scale mineral extraction from geothermal brines, comprehensively evaluating their practicality, environmental considerations, and economic viability.

Table 1: Mineral extraction and recovery methods

Method	Material	Description	Reference
Adsorption	Li, REE	Adsorbent bind target material mostly with hydrogen ions.	Ventura et al. (2018); Park et al. (2012); Farley et al. (1980); Addleman (2015); Noack et al. (2015); Thomas et al. (2015); Thomas et al. (2016); Vulcan Energy Resources; Bauman and Burba (1997); Bauman and Burba (2001); Harrison (2011); Iwanaga et al. (2007)
Ion Exchange	Li, B, Cs, Rb, REE, Zn, Ag, Au	Exchange of similar charged ions between resin (ion exchange material) and brine (solution).	Liu et al., (2019); Shi et al., (2014); Zhou et al., (2020); Ruttinger et al., (2019), SRI International, Standard Lithium, E3 Metals Corp., Anson Resources,
Membrane Separation	Li, SiO ₂	Membrane separation relies on selective permeation of certain components through a semipermeable membrane under pressure	Bourcier et al. (2009); Lu et al., (2018); Li et al., (2019b); Liu et al., (2019); Zhang et al., (2020b); Wang et al., (2020a)
Solvent Extraction	Li, Cs, Rb, REE	Solvent extraction involves the transfer of solutes between immiscible liquid phases through chemical interactions. Suitable for refining due to large quantities of solvent usage.	Belova (2017); McKinley and Ghahreman, (2018); Perez et al., (2019); Liu et al., (2019); Li et al., (2020); Zhou et al., (2020); Wang et al., (2020); Xu et al., (2021); Pure Energy Minerals
Precipitation/Aggregation	Ag, Mn, Au, Pt, Se, As, Cu, Bi, Pb, Zn, Li	Reagents are added to make brine precipitate. Unwanted mineral precipitate and large quantities of reagent usage.	Harrison (2011); Harrison, (2014); Maimoni, (1982); Schultze and Bauer, 1984; Gallup (1992); Christopher et al. (1975)

Electrochemical Separation	B, Li, As, SiO ₂ , Ca, Mg	This method involves the use of electrical potential to drive the migration of ions through an electrolyte solution or across a membrane to move under the influence of an electric field. Techniques such as electrophoresis, electro dialysis, and membrane electrolysis fall under the category of electrochemical separation. suitable for refining than extraction because poor material durability.	Mroczek et al., (2015); Mroczek et al. (2019); McKinley and Ghahreman, (2018); Zhongwei and Xuheng, (2015); Zhu et al., (2018); Xu et al., (2012)
Biochemical Methods	REE, Heavy metals, Li, Au	Biological methods for metal removal from water involve the use of living organisms, such as bacteria, algae, or plants, to sequester, transform, or precipitate metal ions. Microbial Biosorption, Microbial Precipitation, Biological Chelation, Biofiltration are common approaches.	Sedlakova-Kadukova, et al. (2020); Mřážíková, (2016); Brewer, et al. (2019); Lo et al. (2014); Smith et al. (2017)
Hybrid System Combinations	B, Li	Adsorption & Solvent Extraction	Parhi and Sarangi,(2008);Guo et al., (2013); Zante et al., 2020a
	Li	Adsorption & Ultrafiltration	Recepoglu et al., (2017)
	Li	Electrodialysis & Solvent Extraction	Hoshino, (2013); Liu et al.,(2020)

Drawing upon existing literature and established industrial practices, this section offers a concise overview of potential mineral extraction methods for a spectrum of valuable elements from geothermal brines. The elements covered include lithium (Li), cesium (Cs), manganese (Mn), strontium (Sr), neodymium (Nd), stibnite (Sb), copper (Cu), nickel (Ni), zinc (Zn), rubidium (Rb), silver (Ag), and silica (SiO₂).

Neupane and Wendt (2017) conducted a comprehensive analysis of mineral contents and identified potential economic minerals in geothermal brines, focusing on the western region of the United States. Their research suggests that several mineral commodities, including rare-earth elements (REEs), lithium (Li), manganese (Mn), silica (SiO₂), and precious metals, are present in sufficiently high concentrations and flow rates to be economically recoverable. Stringfellow and Dobson (2021) identified inorganic molecular sieve ion-exchange sorbents as the most technologically mature solution, noting that sorbent selectivity, tolerance for interfering ions, and the purity of extracted lithium are key cost drivers. While ion exchange resins and adsorbents are favored for lithium production in geothermal fields, their application can be impeded by low fluid flow rates. Furthermore, elements like silica, magnesium, sodium, calcium, and precipitation inhibitors employed in geothermal plants can damage adsorbents and exacerbate pollution. Additionally, extracting lithium from spent resins/adsorbents incurs further chemical and operating costs. As an alternative, electrodialysis and reverse electrodialysis methods have emerged, but they necessitate dilute fluids, electrical energy, and additional infrastructure alongside geothermal resources. Mroczek et al. (2005) and others (Iwanaga et al., 2007; Park et al., 2012; Chitrakar et al., 2014) highlight the potential of membrane-based techniques like electrodialysis, citing their low energy consumption and high selectivity compared to other electrical methods. This opens avenues for further development and potentially positions electrodialysis as a contender in the mineral extraction landscape alongside traditional methods (e.g., Christopher et al., 1975; Yoshinaga et al., 1984; Rothbaum & Middendorf, 1986; Bauman et al., 2001; Harrison, 2018)

Chemical consumption strategies play a key role in *manganese* extraction from geothermal resources. Notably, selective precipitation with lime and hydroxide-based precipitation at pH 8-9 offer viable options. Furthermore, Harrison (2014) proposed the exploration of combined methodologies, featuring chemical precipitation in silica-free brine following thermal flash processes to produce manganese minerals. These approaches highlight the potential for targeted manganese recovery from geothermal brines with tailored chemical inputs and processing strategies.

Valiente (1999) proposed the utilization of liquid-liquid solvent extraction with di(2-ethyl-hexyl) phosphoric acid (D2EHPA) in hexane for *neodymium* recovery. This approach leverages an ion exchange mechanism to selectively capture neodymium from solution. The choice of D2EHPA as the extractant, combined with hexane as the diluent, capitalizes on the specific chemical properties of both components to achieve efficient and targeted neodymium extraction.

Cesium recovery from geothermal brines can be achieved through diverse strategies, encompassing fractional precipitation, ion exchange, and solvent extraction techniques (Zhang et al., 2020; Schulz and Bray, 1987). Notably, Zhang et al. (2014) demonstrated a promising approach involving the selective removal of cesium from desilicated and defferrified brines through tetrafluoroborate precipitation, often in conjunction with potassium extraction. Broadly, cesium production methods can be categorized into chemical and electrical approaches, highlighting the distinct technological landscapes available for exploiting this valuable element.

Strontium extraction from complex matrices, often alongside other challenging nuclear waste constituents like americium, neptunium, plutonium, uranium, and technetium, has spurred the development of specialized techniques. Horwitz et al. (1990) proposed a solvent extraction process for the co-extraction of cesium and strontium from acidic nitrate media, leveraging the selective affinity of specific extractants towards these elements. This approach offers simultaneous recovery of both valuable resources while simplifying the overall treatment process. Alternatively, Orth and Kurath (1994) explored diversified avenues for strontium extraction. Their work highlights the potential of: (1) chemical solvent extraction with ion exchangers, particularly suited for acidic environments, and (2) precipitation followed by ion exchange, a viable option for alkaline media. These diverse strategies demonstrate the ongoing research efforts towards efficient and targeted strontium recovery from challenging sources.

Antimony, a metalloid with diverse industrial applications, presents a promising target for extraction from geothermal brine. Several promising methodologies have emerged for antimony recovery from geothermal brines: Uysal et al. (2022) demonstrated a highly efficient two-stage cementation process for antimony extraction, achieving a 90% recovery rate. This method leverages the preferential displacement of antimony by zinc from its dissolved state in the brine. Dupont et al. (2016) proposed a comprehensive approach involving grinding, flotation, and density-based separation followed by antimony extraction through chemical, electrochemical, or electrical methods in both alkaline and acidic media. This multifaceted approach caters to the complex composition of geothermal brines and offers versatility in selecting the most effective extraction technique based on specific conditions.

Extracting *copper* from various waste streams and unconventional resources has gained significant interest due to its growing demand and limited primary resources. Several research efforts have explored promising methodologies for copper recovery. Dupont et al. (2016) delve into the intricacies of copper recovery from wastes in conjunction with strontium, offering valuable insights into this area. Barragan (2020) proposes an electrochemical approach for copper extraction following a pickling process. Stando et al. (2021) further showcase the potential of electrochemical techniques by demonstrating copper recovery even in the presence of impurities like iron, magnesium, aluminum, zinc, and arsenic, utilizing carbon nanotubes for enhanced efficiency. Peralta et al. (1996) explore the potential of geothermal sediments as a source of copper, proposing a leaching method for selective separation of arsenic, copper, and zinc. Additionally, Maimoni (1982) investigated the applicability of a liquefied cathode cementation process with metallic iron as the reducing agent for copper recovery from these resources.

For *nickel* recovery, a diverse array of electrochemical methods presents promising avenues, as outlined by Coman et al. (2013). These methodologies can be broadly categorized into several key groups: Separation with chemical precipitators, ion flotation with surfactant, zeolite and ion exchange resins, physisorption, adsorption and electro deionization, electrofloaters and electrocoagulation.

Electrochemical methods such as chemical heavy metal precipitators, ion flotation with the help of surfactants, *zeolite* and ion exchange resins, physisorption (ultra, nano), adsorption and electro deionization, electrofloaters and electrocoagulation are the methods to obtain nickel (Coman et al. 2013).

Several established methods exist for *zinc* extraction from geothermal brines, including lime-induced selective precipitation, liquefied cathode cementation with metallic iron, and precipitation in silica-free brine after flash distillation. Additionally, treating pH-stabilized (calcareous) brine with hydrogen sulfide (H₂S) can be an economical option, as the trace presence of H₂S in geothermal non-condensable gases can reduce the need for external H₂S supply and lower chemical consumption costs.

Chemical and electrochemical methods such as fractional precipitation, ion exchange, solvent extraction are proposed to recover Rubidium (Zhang 2014, 2020).

Several studies have investigated methods for obtaining *silicon dioxide* from various sources. These include techniques for:

- Colloid growth through aging and filtration (Bourcier et al., 2009; Geo40; Roberts, 2009).
- Separation with electrocoagulation (Mroczek et al., 2019; Mohan, 2009).
- Precipitation as calcium silicate and/or metal silicate forms.
- Retention tanks to promote polymer growth (Rothbaum and Anderton, 1976; Shannon et al., 1982; Sasan et al., 2016).

Researchers have proposed cathode cementation with metallic iron and deposition on steel mesh plates for *silver* separation from geothermal sediment (Gallup 1992, Maimoni 1982, Brown and Roberts 1988). However, extracting noble metals like silver often involves energy-intensive hydrometallurgical cycles using acidic or caustic solutions. Fortunately, various methods can be applied to recover such metals from these solutions, including cementation, precipitation, electrolytic recovery, solvent extraction, ion exchange, reductive exchange, adsorption, and even bio-hydrometallurgical approaches like bio-oxidation and biosorption (Syed 2012, Das 2010, Patel et al. 2017).

Western Anatolia hosts a significant geothermal energy potential attributable to its unique geological structure. Numerous electricity generation facilities have been established since 2005, capitalizing on this valuable renewable resource (Figure 1). The installed capacity of these geothermal power plants surpasses 1.7 GWh, with tens of thousands of tons of geothermal fluid produced per hour for electricity generation and subsequent reinjection into the subsurface. Beyond energy production, the extraction of minerals from these geothermal fluids constitutes a developing field of research and discussion.

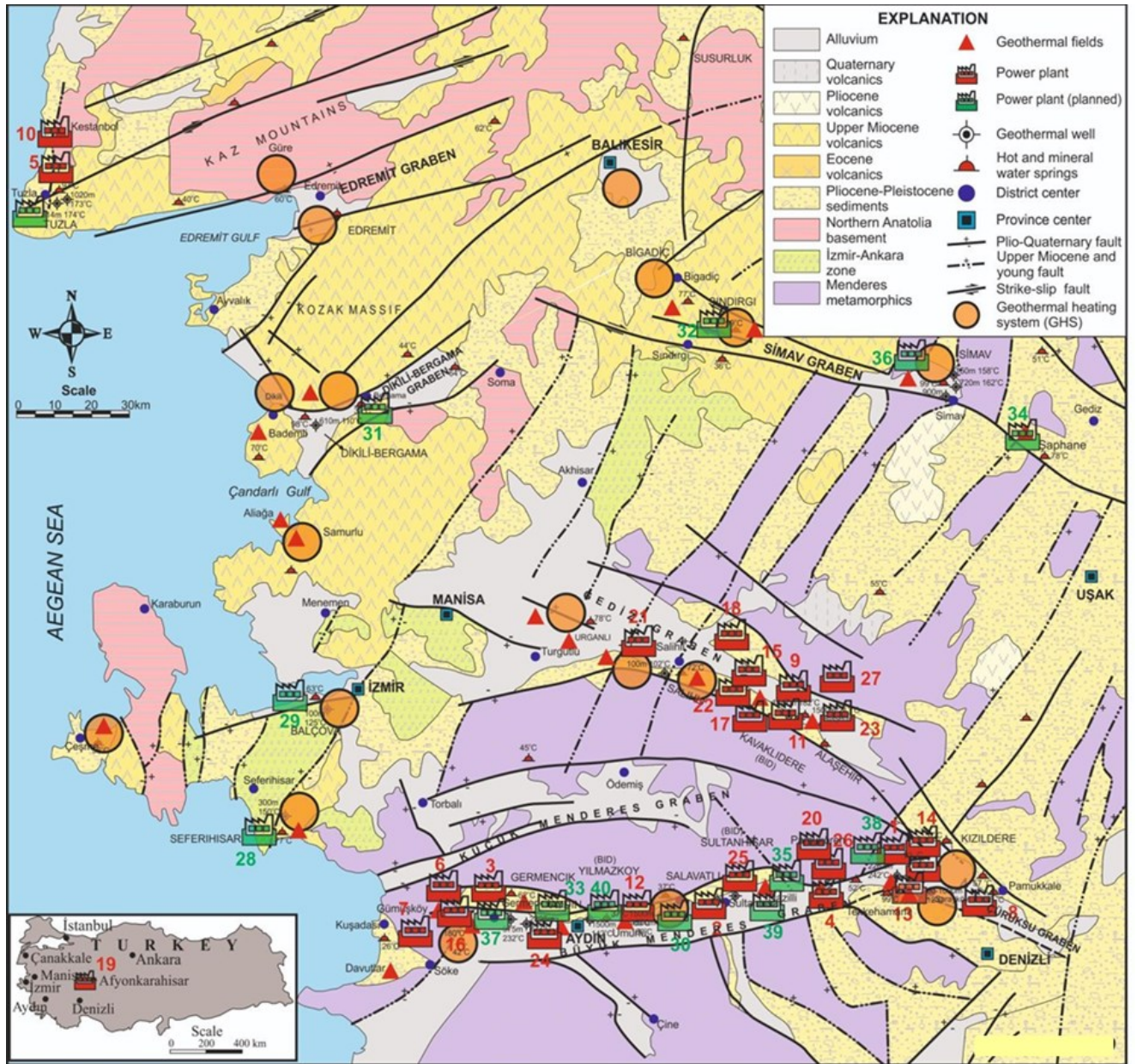


Figure 1: Main geothermal fields of Western Anatolia (Simsek, 2020)

Mineral enrichment within Anatolian metamorphic geothermal reservoirs primarily occurs through the dissolution of reservoir rock during hydrothermal fluid circulation. While the absolute mineral concentrations may be lower compared to globally recognized resources, the significant volume of extracted fluid renders the extraction of even low-concentration minerals potentially economically viable. This study aims to quantify the recoverable reserves of Lithium (Li), Cesium (Cs), Manganese (Mn), Strontium (Sr), Neodymium (Nd), Antimony (Sb), Copper (Cu), Nickel (Ni), Zinc (Zn), Rubidium (Rb), Silver (Ag), and Silica (SiO₂) present within the produced fluids of seven operational geothermal fields: Kızıldere, Germencik, Alaşehir, Salihli, Simav, Seferihisar, and Çanakkale, across Western Anatolia. These fields currently function as sources of electrical and/or thermal energy. The mineral reserve estimation will leverage Monte Carlo simulations, a technique frequently employed in assessing investment decisions for geothermal electricity generation. To achieve this objective, relevant reservoir parameters and water analyses for each location will be compiled and critically assessed from existing literature.

2. MATERIALS AND METHODS

This study focuses on minerals resource assessment within the geothermal fields by using a volumetric approach derived from the U.S. Geological Survey's framework, typically applied to evaluate geothermal energy potential. Subsequently, Muffler (1978) enhanced this method by incorporating a probabilistic approach, termed Monte Carlo simulation, to address uncertainties associated with crucial reservoir parameters, including area and thickness. This study adapted Monte Carlo simulation to quantify the minerals potential of geothermal systems. At its core, the volumetric method hinges upon calculating the in-situ mineral content within the geothermal brine occupying the reservoir's porous and fractured media. Notably, the potential contribution of minerals residing within the rock matrix was not considered, and potential minerals transfer from rock grains to brine due to concentration gradients during production was deemed negligible. Aydin et al. (2022) used equation (1) for assessment of lithium. This study benefits from this equation to assess mineral reserves in western Anatolia.

$$\text{Recoverable mineral} = A \times h \times \phi \times C \times RF \times E \quad (1)$$

where, "A": reservoir area (km²); "h": reservoir thickness (m); "φ": equivalent porosity (fraction); C: mineral concentration in brine (ppm); RF: Recovery Factor (fraction); E: Extraction efficiency.

The estimation of recovery factors for geothermal reservoirs remains a debated subject, with research predominantly focused on energy extraction (DiPippo, 2007; Lawless and Beardmore, 2010; Zarrouk and Moon, 2014). Consequently, this study will utilize reported recovery factors ranging from 5% to 24%, reflecting the impact of porosity, and permeability (Williams et al., 2008; Avsar et al., 2015). However, geothermal brine mineral extraction efficiency additionally depends on the chosen capture technique, often resulting in incomplete recovery of target minerals. Therefore, to account for this variability, this study integrates experimentally determined mineral extraction efficiencies as multipliers alongside the recovery factors. For instance, Zhang et al. (2021) and Sun et al. (2020) proposed an iron phosphate electrochemical method for environmentally friendly lithium recovery, achieving a maximum extraction efficiency of 90.65%. Similarly, Harrison (2014) reported lithium extraction exceeding 95% in laboratory experiments using sorbents. Conversely, McEachern et al. (2020) observed efficiencies below 60% with aluminate-based adsorbents. Moreover, McGrail et al. (2017) and Smith et al. (2017) documented rare earth element extraction efficiencies approaching 90% alongside recovery efficiencies of approximately 20%. Values for key reservoir characteristics, such as porosity, thickness, and areal extent, were obtained from relevant references.

Due to inherent uncertainties associated with reservoir parameters utilized in the volumetric method, a Monte Carlo simulation approach is employed for robust estimation. This probabilistic technique relies on iteratively sampling random values for key parameters, such as porosity or thickness, from predefined probability distributions. Subsequently, for each iteration, the production potential is calculated, generating a range of possible outcomes. By analyzing the distribution of these outcomes, uncertainty associated with the estimated reserve is significantly reduced and a more representative understanding of the resource potential is achieved. Due to lack of data distribution, we selected triangular distribution for all uncertain parameters.

3. RESULTS AND DISCUSSIONS

Western Anatolia hosts rich geothermal provinces characterized by numerous high-temperature fields distributed across distinct tectonic grabens. Notably, Kızıldere and Germencik fields lie within the Büyük Menderes Graben the prominent, while the Gediz Graben hosts the Alaşehir and Salihli fields. Furthermore, the Seferihisar Field resides within the Çubukdağ Graben, and the Simav Graben encompasses the Eynal, Naşa, and Çitgöl fields. Finally, the Edremit Graben is distinguished by the presence of the Tuzla Field.

3.1 Kızıldere Geothermal Field

Located at the easternmost and narrowest extremity of the Büyük Menderes Graben, the Kızıldere Geothermal Field holds the distinction of being the first field discovered in Turkey for geothermal electricity generation. The field is underlain by the Menderes Massif, a metamorphic complex composed of diverse schists and marbles (including schist, quartzite, mica schist, and chlorite schist). These formations contribute to the production of geothermal fluids with temperatures reaching 245 °C. Kızıldere boasts a well-developed infrastructure, with over a hundred wells drilled to date and an installed capacity exceeding 280.85 MWe. Further details regarding the reservoir characteristics and relevant mineral concentrations for this study are available in Table 2.

Table 2: Data input values for reserve estimation of Kızıldere geothermal field.

Parameter	Units	Mineral Concentrations	Min.	Mean	Max.	Reference
Reservoir Area	A (m²)		30000000	70000000	10000000	Yilmazer (2015)
Reservoir Thickness	H (m)		500	1000	1500	Yilmazer (2015)
Equivalent Porosity	Θ (%)		3	5	10	Aydın and Akın (2020); Küçük (2018)
Lithium -Li	C (ppm)	5.7	0.57	5.7	8.55	Haklıdır etal. (2021)
Neodymium-Nd	C (ppm)	1.3	0.13	1.3	1.95	Möller etal. (2004)
Cesium-Cs	C (ppm)	0.02	0.002	0.02	0.03	Bundschuh etal. (2013)
Manganese-Mn	C (ppm)	0.54	0.054	0.54	0.81	Zorlu (2022)
Strontium-Sr	C (ppm)	0.4	0.04	0.4	0.6	Zorlu (2022)
Antimony-Sb	C (ppm)	0.18	0.018	0.18	0.27	Zorlu (2022)
Copper-Cu	C (ppm)	0.5	0.05	0.5	0.75	Zorlu (2022)
Nickel-Ni	C (ppm)	2.16	0.216	2.16	3.24	Zorlu (2022)
Zinc-Zn	C (ppm)	0.09	0.009	0.09	0.135	Zorlu (2022)
Rubidium- Rb	C (ppm)	Below detection limit	0.001	0.01	0.015	Bundschuh etal. (2013)
Silica- SiO ₂	C (ppm)	560	56	560	840	Haklıdır etal. (2021)
Silver-Ag	C (ppm)	0.93	0.093	0.93	1.395	Zorlu (2022)
Recovery Factor	RF (%)		10	15	20	Williams etal. (2008); Avsar etal. (2015)
Extraction Efficiency	E (%)		50	70	90	Sun etal. (2020); Meechem etal. (2020); McGrail vd. (2017); Smith etal. (2019)

3.2 Alaşehir Geothermal Field

Located on the southern side of the Gediz Graben, Alaşehir geothermal field harness its geothermal potential from Meta-sedimentary units, marbles and fractured quartzite zones in the Paleozoic-Mesozoic aged Menderes Metamorphites (Rabet et al., 2017). Reservoir temperature ranges from 150 to 220 °C and reservoir fluid is water-dominated (Baba, 2015). The total installed capacity of geothermal power plants in the area is 310 MWe. The reservoir characteristics of Alaşehir Geothermal Field and the precious mineral concentrations to be used in the study are given in Table 3.

Table 3: Data input values for reserve estimation of Alaşehir geothermal field.

Parameter	Units	Mineral Concentrations	Min.	Mean	Max.	Reference
Reservoir Area	A (m²)		45000000	90000000	135000000	Yilmazer (2015)
Reservoir Thickness	H (m)		250	500	750	Yilmazer (2015)
Equivalent Porosity	Θ (%)		3	5	10	Aydın and Akın (2020); Küçük (2018)
Lithium -Li	C (ppm)	6.3	0.63	6.3	9.45	Haklıdır and Şengün (2020)
Neodymium-Nd	C (ppm)	-	0.275	2.75	4.125	Salihli value used.
Cesium-Cs	C (ppm)	0.01	0.001	0.01	0.015	Bundschuh etal. (2013)
Manganese-Mn	C (ppm)	0.08	0.008	0.08	0.12	Bundschuh etal. (2013)
Strontium-Sr	C (ppm)	0.2	0.02	0.2	0.3	Bundschuh etal. (2013)
Antimony-Sb	C (ppm)	0.005	0.0005	0.005	0.0075	Bundschuh etal. (2013)
Copper-Cu	C (ppm)	0.9	0.09	0.9	1.35	Zorlu (2022)
Nickel-Ni	C (ppm)	-	0.95	9.5	14.25	Salihli value used.
Zinc-Zn	C (ppm)	0.01	0.001	0.01	0.015	Bundschuh etal. (2013)

Rubidium- Rb	C (ppm)	0.01	0.001	0.01	0.015	Bundschuh etal. (2013)
Silica- SiO ₂	C (ppm)	0.01	36.6	366	549	Haklıdır and Şengün (2020)
Recovery Factor	RF (%)	366	10	15	20	Williams etal.(2008); Aysar etal. (2015)
Extraction Efficiency	E (%)		50	70	90	Sun etal. (2020); Mceachem etal. (2020); McGrail vd. (2017); Smith etal. (2019)

3.3 Salihli Geothermal Field

It is located within the Gediz Graben, where the metamorphic rocks of the Menderes Massif function as aquifers for both cold and thermal waters. The metamorphites of the Menderes Massif serve as aquifers for both cold and thermal waters. The Neogene terrestrial sediments serve as caprock. Notably, the Salihli-Köseali geothermal well yielded the second-highest reservoir temperature recorded in Turkey, reaching a remarkable 287°C. Further details regarding the reservoir characteristics of the Salihli Geothermal Field and the specific mineral concentrations relevant to the study are presented in Table 4.

Table 4: Data input values for reserve estimation of Salihli geothermal field.

<u>Parameter</u>	<u>Units</u>	<u>Mineral Concentrations</u>	<u>Min.</u>	<u>Mean</u>	<u>Max.</u>	<u>Reference</u>
Reservoir Area	A (m ²)		5000000	12000000	20000000	Yilmazer (2015)
Reservoir Thickness	H (m)		250	500	750	Yilmazer (2015)
Equivalent Porosity	Θ (%)		3	5	10	Aydın and Akın (2020); Küçük (2018)
Lithium -Li	C (ppm)	5.14	0.514	5.14	7.71	Özen vd. (2010)
Neodymium-Nd	C (ppm)	2.27	0.227	2.27	3.405	Möller etal. (2004)
Cesium-Cs	C (ppm)	0.03	0.003	0.03	0.045	Bundschuh etal. (2013)
Manganese-Mn	C (ppm)	0.01	0.001	0.01	0.015	Bundschuh etal. (2013)
Strontium-Sr	C (ppm)	0.06	0.006	0.06	0.09	Bundschuh etal. (2013)
Antimony-Sb		0.001	1E-04	0.001	0.0015	Bundschuh etal. (2013)
Copper-Cu	C (ppm)	9.5	0.95	9.5	14.25	Özen etal. (2010)
Nickel-Ni	C (ppm)	4.3	0.43	4.3	6.45	Özen etal. (2010)
Zinc-Zn	C (ppm)	0.02	0.002	0.02	0.03	Bundschuh etal. (2013)
Rubidium- Rb	C (ppm)	Below detection limit	0.001	0.01	0.015	Bundschuh etal. (2013)
Silica- SiO ₂	C (ppm)	322	32.2	322	483	Özen etal. (2010)
Silver-Ag	C (ppm)	0.88	8.80E-02	0.88	1.32	Özen etal. (2010)
Recovery Factor	RF (%)		10	15	20	Williams etal.(2008); Aysar etal. (2015)
Extraction Efficiency	E (%)		50	70	90	Sun etal. (2020); Mceachem etal. (2020); McGrail vd. (2017); Smith etal. (2019)

3.3 Germencik Geothermal Field

Germencik geothermal field is in the west of the Büyük Menderes Graben and composed of two reservoirs. The primary reservoir is constituted by the fractured quartz schists, gneisses, and marbles of the Menderes Massif. In contrast, the secondary reservoir is composed of Neogene-aged sandstones and conglomerates. Neogene-aged clay-bearing sedimentary units serve as the caprock for the entire system. Recorded temperatures within the field range from 200°C to 232°C, as reported by Filiz et al. (2000). Notably, the installed capacity of geothermal power plants found between Ömerbeyli and Gümüşköy collectively reaches 502 MWe. Table 5 provides a comprehensive overview of the reservoir characteristics of the Germencik Geothermal Field and the specific precious mineral concentrations relevant to the present study.

Table 5: Data input values for reserve estimation of Germencik geothermal field.

Parameter	Units	Mineral Concentrations	Min.	Mean	Max.	Reference
Reservoir Area	A (m²)		75000000	150000000	225000000	Yilmazer (2015)
Reservoir Thickness	H (m)		171	1000	1400	Yilmazer (2015)
Equivalent Porosity	Θ (%)		3	5	7.5	Aydın and Akın (2020); Küçük (2018)
Lithium -Li	C (ppm)	10.6	1.06	10.6	15.9	Karakuş and Şimşek (2013)
Neodymium-Nd	C (ppm)	347.4	34.74	347.4	521.1	Möller et al. (2004)
Cesium-Cs	C (ppm)	0.06	0.006	0.06	0.09	Bundschuh et al. (2013)
Manganese-Mn	C (ppm)	0.15	0.015	0.15	0.225	Parkın (2012)
Strontium-Sr	C (ppm)	0.11	0.011	0.11	0.165	Bundschuh et al. (2013)
Antimony-Sb	C (ppm)	1.9	0.19	1.9	2.85	Parkın (2012)
Copper-Cu	C (ppm)	0.079	7.90E-03	0.079	0.1185	Parkın (2012)
Nickel-Ni	C (ppm)	0.26	0.026	0.26	0.39	Bundschuh et al. (2013)
Zinc-Zn	C (ppm)	0.29	0.029	0.29	0.435	Parkın (2012)
Rubidium- Rb	C (ppm)	0.03	0.003	0.03	0.045	Bundschuh et al. (2013)
Silica- SiO ₂	C (ppm)	535	53.5	535	802.5	Karakuş and Şimşek (2013)
Recovery Factor	RF (%)		10	15	20	Williams et al. (2008); Avsar et al. (2015)
Extraction Efficiency	E (%)		50	70	90	Sun et al. (2020); Meechem et al. (2020); McGrail vd. (2017); Smith et al. (2019)

3.4 Seferihisar Geothermal Field

Seferihisar geothermal field is located in the southwest of Izmir. The rhyolites and rhyolodacites within the Cumaovası Volcanites, identified as the heat source. These volcanic domes, situated as individual features within the Cretaceous formations southeast of the Graben, contribute significant thermal energy. Fractured mafic submarine volcanites and highly permeable limestone and serpentinite masses of the Bornova mélange serve as the reservoir rocks, while relatively impermeable clay-rich zones and sandstone and shale levels of Neogene sediments act as cap rocks. The reservoir fluid is predominantly liquid, and its temperature varies between 70°C and 200°C depending on depth. The field boasts a single geothermal power plant with a capacity of 12 MWe. Table 6 details the reservoir characteristics and relevant mineral concentrations of the Seferihisar Geothermal Field.

Table 6: Data input values for reserve estimation of Seferihisar geothermal field

Parameter	Units	Mineral Concentrations	Min.	Mean	Max.	Reference
Reservoir Area	A (m²)		12500000	25000000	37500000	Aydın et al. (2022)
Reservoir Thickness	H (m)		500	1000	1500	Aydın et al. (2022)
Equivalent Porosity	Θ (%)		3	5	10	Aydın and Akın (2020); Küçük (2018)
Lithium -Li	C (ppm)	10	1	10	15	Zorlu (2020)
Neodymium-Nd	C (ppm)	-	0.000092	0.00092	0.00138	no analysis, value estimated
Cesium-Cs	C (ppm)	0.15	0.015	0.15	0.225	Bundschuh et al. (2013)
Manganese-Mn	C (ppm)	0.19	0.019	0.19	0.285	Bundschuh et al. (2013)
Strontium-Sr	C (ppm)	Below detection limit	0.005	0.05	0.075	Bundschuh et al. (2013), The measurement limit is accepted as the value.
Antimony-Sb	C (ppm)	0.001	0.00001	0.0001	0.00015	Bundschuh et al. (2013)
Copper-Cu	C (ppm)	-	0.0001	0.001	0.0015	no analysis, value estimated
Nickel-Ni	C (ppm)	0.12	0.012	0.12	0.18	Bundschuh vd. (2013)
Zinc-Zn	C (ppm)	0.02	0.002	0.02	0.03	Bundschuh vd. (2013)
Rubidium- Rb	C (ppm)	Below detection limit	0.001	0.01	0.015	Bundschuh et al. (2013), The measurement limit is accepted as the value.
Silica- SiO ₂	C (ppm)	119	11.9	119	178.5	Zorlu (2020)

Recovery Factor	RF (%)		10	15	20	Williams et al. (2008); Avsar et al. (2015)
Extraction Efficiency	E (%)		50	70	90	Sun et al. (2020); Meechem et al. (2020); McGrail et al. (2017); Smith et al. (2019)

3.5 Simav Geothermal Field

Simav geothermal field is in the central part of the Simav Graben. The primary reservoir rocks within the field are the chalcocite and marble levels of the Kirkbudak formation. Naş basalts potentially contribute as secondary reservoir rocks. Impervious Neogene rocks such as claystone, sandstone and conglomerate cover the Simav Geothermal System (Gemici and Tarcen, 2002; MTA, 2005). The reservoir temperature ranges between 180°C and 200°C. Carbonate minerals, as observed by Gemici and Tarcen (2002), tend to precipitate in the region. Table 7 presents the detailed reservoir characteristics and relevant mineral concentrations of the Simav geothermal field.

Table 7: Data input values for reserve estimation of Simav geothermal field

Parameter	Units	Mineral Concentrations	Min.	Mean	Max.	Reference
Reservoir Area	A (m ²)		1000000	2000000	5000000	Karakuş et al. (2017)
Reservoir Thickness	H (m)		250	1000	3000	Karakuş et al. (2017)
Equivalent Porosity	Θ (%)		6	6	6	Karakuş et al. (2017)
Lithium -Li	C (ppm)	1.76	0.176	1.76	2.64	Çardak et al. (2019)
Neodymium-Nd	C (ppm)	-	0.000092	0.00092	0.00138	no analysis, value estimated
Cesium-Cs	C (ppm)	0.02	0.002	0.02	0.03	Bundschuh et al. (2013)
Manganese-Mn	C (ppm)	15.25	1.525	15.25	22.875	Çardak et al. (2019)
Strontium-Sr	C (ppm)	0.05	0.005	0.05	0.075	Bundschuh et al. (2013)
Antimony-Sb	C (ppm)	0.002	0.0002	0.002	0.003	Bundschuh et al. (2013)
Copper-Cu	C (ppm)	-	1.00E-04	0.001	0.0015	no analysis, value estimated
Nickel-Ni	C (ppm)	15.25	1.525	15.25	22.875	Çardak et al. (2019)
Zinc-Zn	C (ppm)	5.5	0.55	5.5	8.25	Çardak et al. (2019)
Rubidium- Rb	C (ppm)	0.01	0.001	0.01	0.015	Bundschuh et al. (2013)
Silica- SiO ₂	C (ppm)	280.7142857	28.1	281	421.5	Çardak et al. (2019)
Recovery Factor	RF (%)		10	15	20	Williams et al. (2008); Avsar et al. (2015)
Extraction Efficiency	E (%)		50	70	90	Sun et al. (2020); Meechem et al. (2020); McGrail et al. (2017); Smith et al. (2019)

3.6 Çanakkale Tuzla Geothermal Field

Çanakkale-Tuzla geothermal field is located in the Edremit Graben of northwestern Turkey, lies 80 km southwest of Çanakkale and 5 km from the Aegean Sea. Influenced by seawater infiltration, its thermal waters exhibit Na-Cl and Na-HCO₃-Cl types, reaching well temperatures of 173°C. The installed geothermal power plants' capacity is 46.5 MWe in the region. The reservoir rocks are composed of different types of lavas and recrystallized limestones of the metamorphic basement, while the tuffaceous claystone, conglomerate and sandstones above these units serve as caprocks for the system (Gevrek et al., 1984; MTA, 2005). The reservoir characteristics of Tuzla Geothermal Field and the mineral concentrations to be used in the study are given in Table 8.

Table 8: Data input values for reserve estimation of Çanakkale Tuzla geothermal field

Parameter	Units	Mineral Concentrations	Min.	Mean	Max.	Reference
Reservoir Area	A (m ²)		3000000	6000000	9000000	Yilmazer (2015)
Reservoir Thickness	H (m)		250	500	750	Yilmazer (2015)
Equivalent Porosity	Θ (%)		3	5	10	Aydın and Akın (2020); Küçük (2018)
Lithium -Li	C (ppm)	29.294	2.9294	29.294	43.941	Katircioğlu (2013)
Neodymium-Nd	C (ppm)	0.00092	0.000092	0.00092	0.00138	Özçetin and Gemici (2018)

Cesium-Cs	C (ppm)	2.4	0.24	2.4	3.6	Özçetin and Gemici (2018)
Manganese-Mn	C (ppm)	5.117	0.5117	5.117	7.6755	Katircioğlu (2013)
Strontium-Sr	C (ppm)	169.968	17	170	255	Katircioğlu (2013)
Antimony-Sb	C (ppm)	<2	0.19	1.9	2.85	Karaca et al. (2013)
Copper-Cu	C (ppm)	2.4	2.40E-01	2.4	3.6	Özçetin (2018)
Nickel-Ni	C (ppm)	<0.3	0.02	0.2	0.3	Karaca et al. (2013)
Zinc-Zn	C (ppm)	0.535	0.0535	0.535	0.8025	Karaca et al. (2013)
Rubidium- Rb	C (ppm)	0.026	0.0026	0.026	0.039	Karaca et al. (2013)
Silica- SiO ₂	C (ppm)	96.2	9.62	96.2	144.3	Özçetin (2018)
Recovery Factor	RF (%)		10	15	20	Williams et al. (2008); Avsar et al. (2015)
Extraction Efficiency	E (%)		50	70	90	Sun et al. (2020); Mceachem et al. (2020); McGrail vd. (2017); Smith et al. (2019)

Based on extensive data collated from the literature, reserve estimations for Western Anatolia indicate a high potential for mineral wealth. Lithium exhibits the most substantial reserve projection, exceeding 24,813 metric tons. Significant reserves of other vital elements are also evident, including 208 metric tons of manganese, 67,423 metric tons of neodymium, 35 metric tons of cesium, 924 metric tons of strontium, 412 metric tons of antimony, 958 metric tons of copper, 553 metric tons of nickel, 113 metric tons of zinc, 8 metric tons of rubidium, and a remarkable 246,417 metric tons of silica. Additionally, estimated silver reserves reach 844 metric tons (Table 9). These findings highlight the remarkable geological diversity and mineral resource potential of Western Anatolia. The probabilistic results of mineral reserve estimation are shown in the Appendix in the figure 2 through figure 8 as cumulative probability density function.

Table 9: Estimated reserves (P10, 90%) of high-temperature geothermal fields in Western Anatolia

	Seferihisar field	Alaşehir field	Germencik field	Kızıldere field	Simav field	Salihli field	Tuzla field	Total
Lithium -Li	414	723	1964	986	1039	5116	14572	24813
Manganese-Mn	8	5	25	80	65	0.1	24	208
Neodymium-Nd	0.04	205	67004	194	0.01	21	0.004	67423
Cesium-Cs	7	1	11	4	0.1	0.3	12	35
Strontium-Sr	2	15	20	69	0.2	1	816	924
Antimony-Sb	0.004	0.37	372	31	0.012	0.009	9	412
Copper-Cu	0.04	752	14	84	0.006	96	12	958
Nickel-Ni	5	1	52	371	81	42	1	553
Zinc-Zn	1	1	58	15	35	0	3	113
Rubidium- Rb	0.41	0.74	5.21	1.73	0.05	0.1	0.14	8
Silica- SiO ₂	5181	26242	107511	102208	1600	3171	504	246417
Silver-Ag	0.188	302	1	491	0.042	48	2	844

3.7 Economical Analysis of Mineral Extraction

While numerous critical minerals reside within geothermal brines, lithium gained prominent attention due to its extensive research and diverse applications. Direct Lithium Extraction (DLE) techniques, primarily those leveraging adsorption and ion-exchange, find wide applicability in lithium extraction from geothermal sources. Warren (2021) estimates production costs for extracting lithium from brines containing 100-400 ppm to range from 3200 to 4554 USD/mt Li in the US/Europe, with a 5-year payback period. Notably, for Western Turkey's brines, the extraction cost stands at 4.6 USD/kg Li, with a 12-year payback period.

Extracting various critical minerals, not just lithium, from geothermal fluids presents a cost-effective and environmentally friendly approach to raw material production. This viability directly hinges on the mineral concentration within the brine and the employed technology. Notably, geothermal brine extraction offers an effective strategy to mitigate supply chain risks associated with critical minerals.

The International Energy Agency emphasizes the crucial role of critical minerals like copper, lithium, nickel, cobalt, and rare earths in fueling clean energy technologies, including wind turbines, power grids, electric vehicle batteries, LEDs, and hydrogen electrolyzers. Demand for these minerals is expected to soar as clean energy transitions gain momentum. Securing sustainable and reliable sources for materials crucial for daily and industrial needs is paramount. Utilizing geothermal resources for critical mineral extraction presents a promising avenue towards economic feasibility in this endeavor.

In 2022, the U.S. Geological Survey (USGS) released a report outlining short- and medium-term requirements for critical minerals essential for energy production and various industrial applications. According to the report, six materials - cobalt, dysprosium, gallium, natural graphite, iridium, and neodymium - are categorized as "critical" in the short term. Notably, the medium-term outlook includes 12 critical, 6 near critical, and 4 noncritical materials. Key points include elevated importance to energy for copper and silicon while maintaining their supply risk. Additionally, supply risk scores increase for aluminum, iridium, manganese, neodymium, phosphorus, platinum, and silicon carbide, despite their stable importance to energy. Nickel exhibits simultaneous increases in both importance to energy and supply risk. Conversely, dysprosium experiences a decline in energy importance due to potential substitutes in the medium term, but its supply risk rises, solidifying its status as a critical material.

While the individual element concentrations within the geothermal brines of western Anatolia are demonstrably lower when compared to global benchmarks, their cumulative economic significance cannot be disregarded solely based on individual values. As evidenced in Table 10, the combined resource base extracted from these production fields encompasses 25,000 tons of lithium, 208 tons of manganese, 67,000 metric of neodymium, 35 tons of cesium, 924 tons of strontium, 412 tons of antimony, 958 tons of copper, 553 tons of nickel, 113 tons of zinc, 8 tons of rubidium, 844 tons of silver, and 246,000 tons of silica. Notably, the estimated total economic value associated with these extracted minerals surpasses 28 billion USD (Table 10).

Table 10: Economic value of mineral assets in geothermal reservoirs in west of Turkey

Mineral ID	Estimated reserve (ton)	Market price (USD/ton)	Explanation	Estimated Economic Value (USD)
Lithium -Li	24,813	\$846,220	Metal (Li \geq 99%)	\$20,997,244,454
Manganese-Mn	208	\$937	Manganese Sulfate(Mn= %32)	\$608,810
Neodymium-Nd	67,423	\$19,848	Metal (Nd=99,0-99,9%)	\$1,338,225,654
Cesium-Cs	35	\$101,258,846	Cs \geq 99,5%	\$3,544,059,610
Strontium-Sr	924	\$4,340	Al-Sr (%10) Alloy	\$40,097,812
Antimony-Sb	412	\$133,800	Sb-05 (\geq 99,999%)	\$55,125,600
Copper-Cu	958	\$11,070	Powder Copper	\$10,605,060
Nickel-Ni	553	\$3,879	Nikel (Ni: 99,90%)	\$2,144,983
Zinc-Zn	113	\$483	Zinc (Zn \geq 99,5%)	\$54,623
Rubidium- Rb	8	\$115,724,345	Rubidium (Rb \geq 99,995%)	\$925,794,760
Silica- SiO ₂	246,417	\$805	Si \geq 97%, Fe \geq 1,8%,Ca \geq 1,0%	\$198,401,020
Silver-Ag	844	\$771,000	99,99%	\$650,724,000
Total				<u>27.763.086.384</u>

4. CONCLUSION

Extracting critical minerals from geothermal brines presents an economical viable and environmentally friend approach to securing essential raw materials for both daily needs and clean energy technologies. Mineral enrichment within Anatolian metamorphic geothermal reservoirs primarily occurs through the dissolution of reservoir rock during hydrothermal fluid circulation. This study quantified the recoverable reserves of Lithium (Li), Cesium (Cs), Manganese (Mn), Strontium (Sr), Neodymium (Nd), Antimony (Sb), Copper (Cu), Nickel (Ni), Zinc (Zn), Rubidium (Rb), Silver (Ag), and Silica (SiO₂) present within the produced fluids of seven operational geothermal

fields: Kızıldere, Germencik, Alaşehir, Salihli, Simav, Seferihisar, and Çanakkale, across Western Anatolia. The study employed Monte Carlo simulations to overcome uncertainty of parameters such as concentration, area, and thickness. Based on extensive data collated from the literature, reserve estimations for Western Anatolia indicate a high potential for mineral wealth. Lithium exhibits the most substantial reserve projection, exceeding 24,813 metric tons. Significant reserves of other vital elements are also evident, including 208 metric tons of manganese, 67,423 metric tons of neodymium, 35 metric tons of cesium, 924 metric tons of strontium, 412 metric tons of antimony, 958 metric tons of copper, 553 metric tons of nickel, 113 metric tons of zinc, 8 metric tons of rubidium, and a remarkable 246,417 metric tons of silica. Additionally, estimated silver reserves reach 844 metric tons. These findings highlight the remarkable geological diversity and mineral resource potential of Western Anatolia. While the absolute mineral concentrations may be lower compared to globally recognized resources, the significant volume of extracted fluid renders the extraction of even low-concentration minerals potentially economically viable. Careful consideration of mineral concentrations within the brine and the selection of appropriate technologies are crucial for economic feasibility. Moving forward, research and development efforts should focus on optimizing extraction processes and mitigating environmental impacts to fully unlock the potential of geothermal brines as a sustainable source of critical minerals.

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APPENDIX

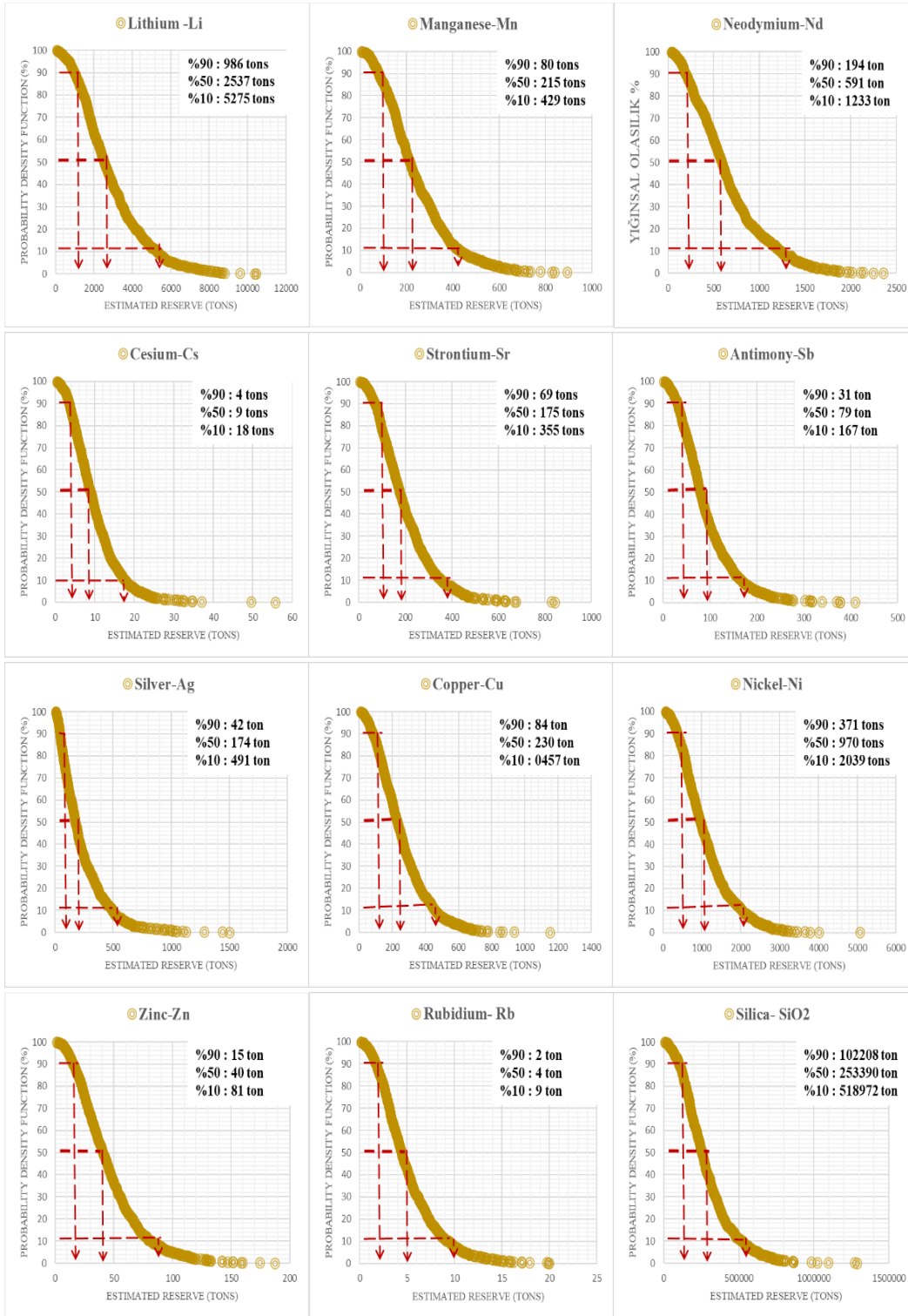


Figure 2: Mineral reserve estimation of Kızıldere geothermal field.

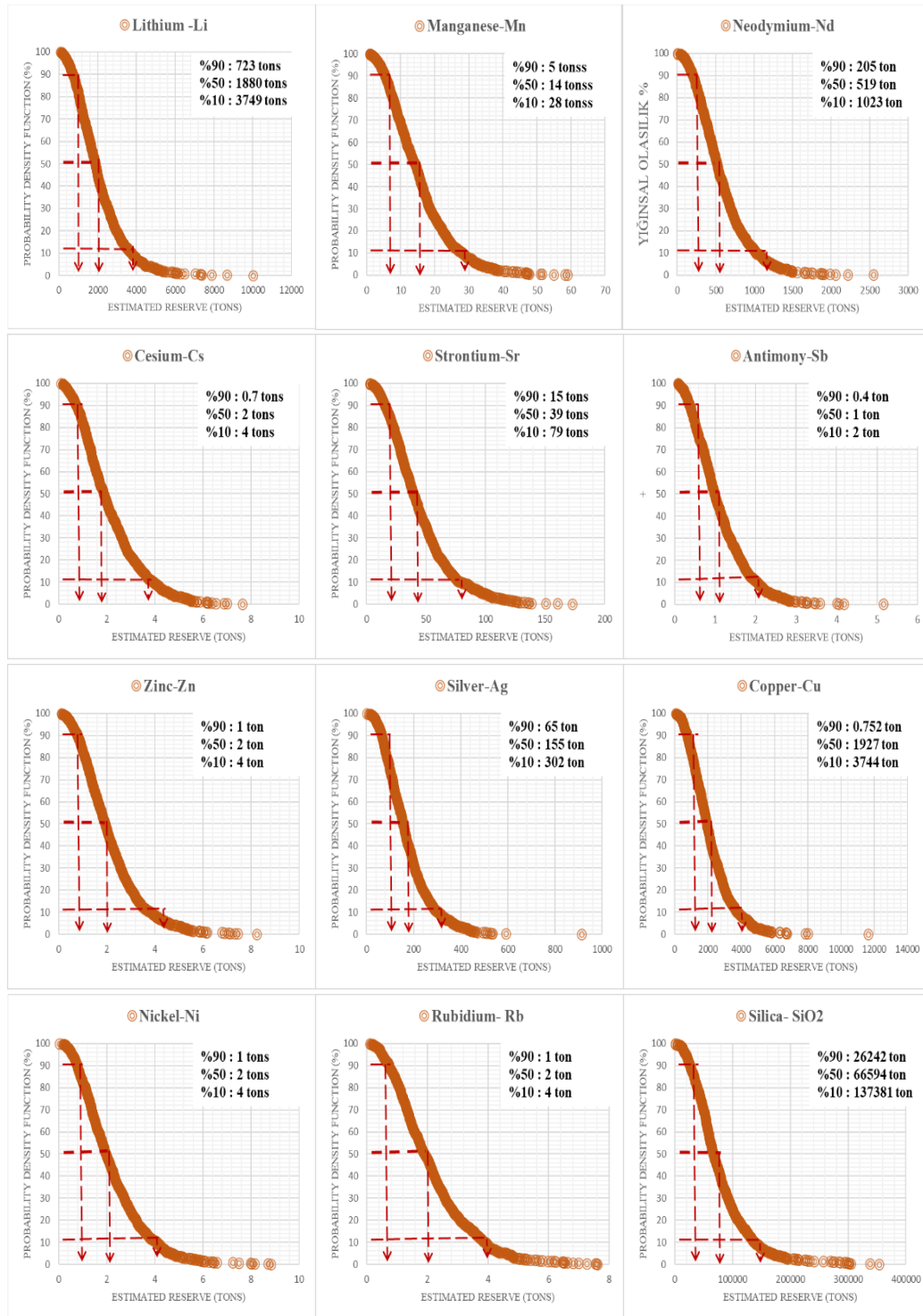


Figure 3: Mineral reserve estimation of Alaşehir geothermal field.

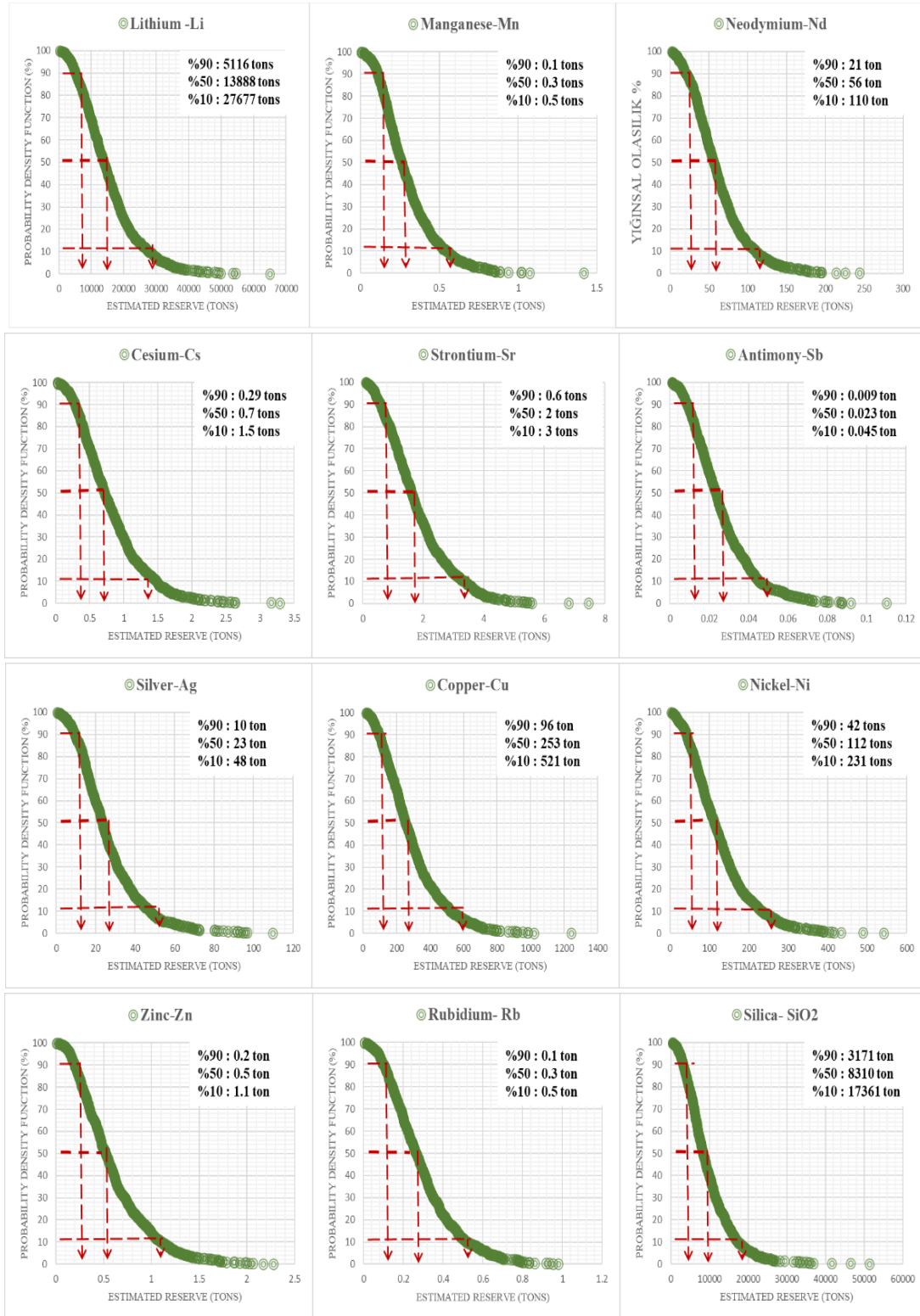


Figure 4: Mineral reserve estimation of Salihli geothermal field.

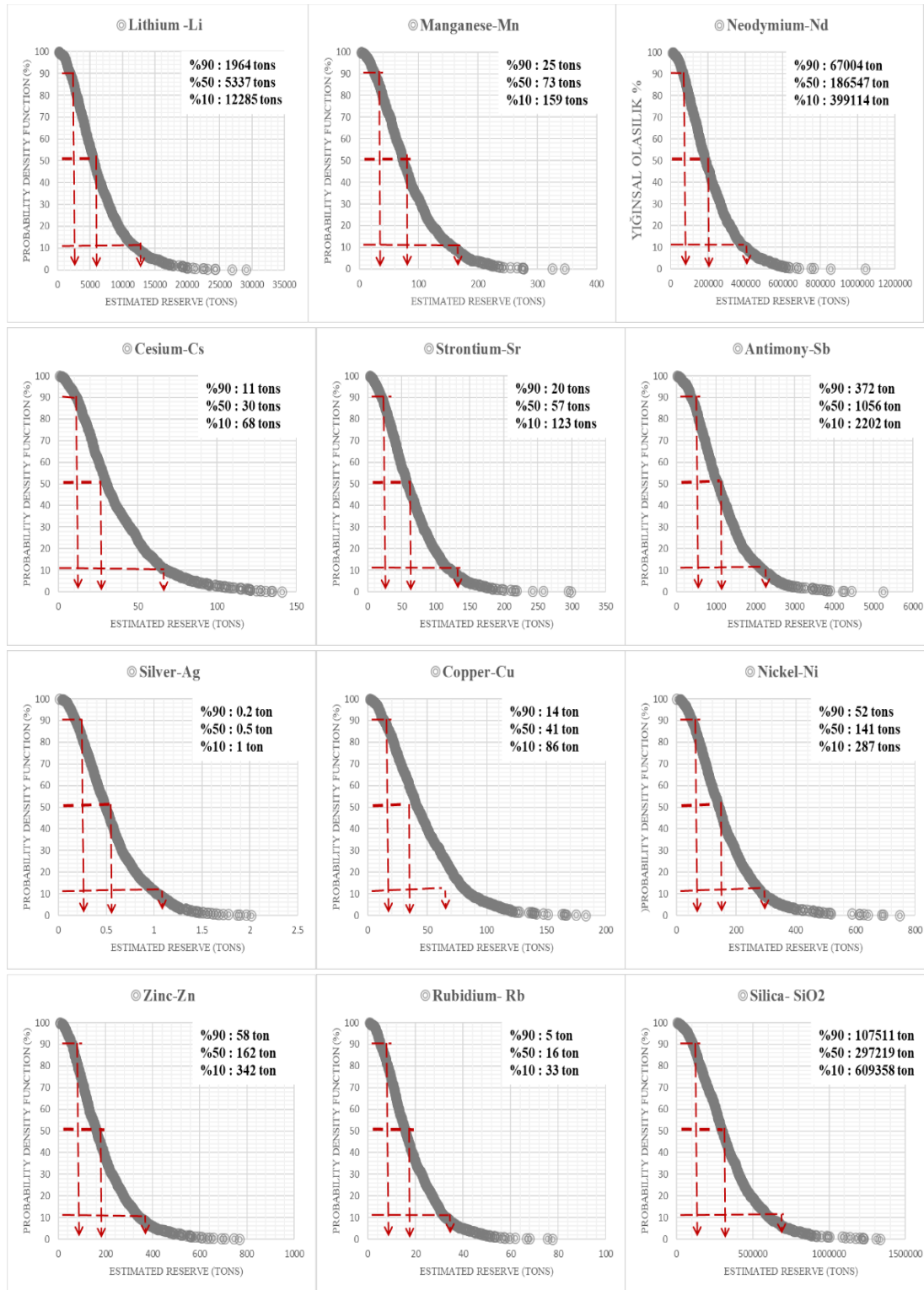


Figure 5: Mineral reserve estimation of Germencik geothermal field.

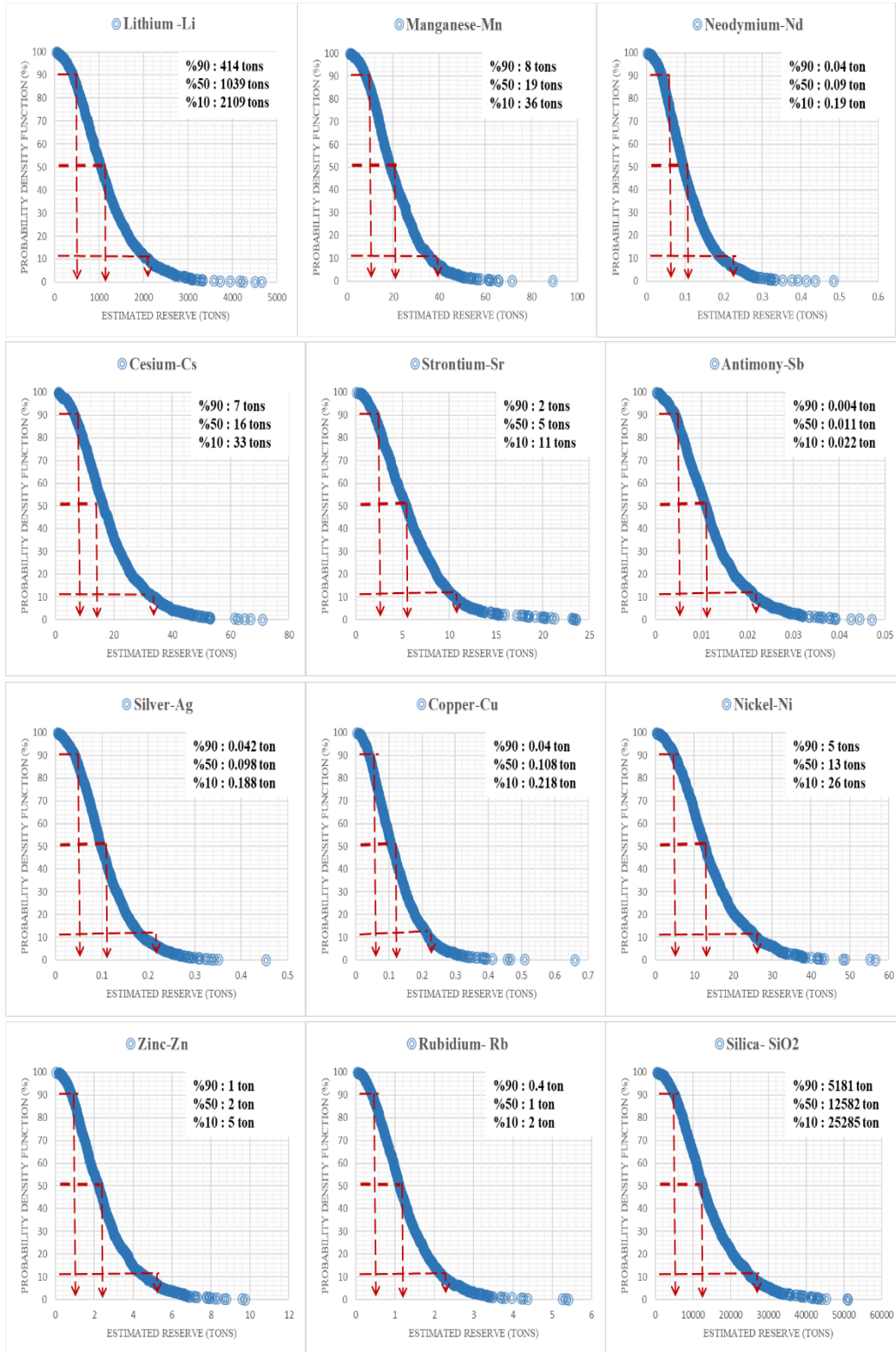


Figure 6: Mineral reserve estimation of Seferihisar geothermal field.

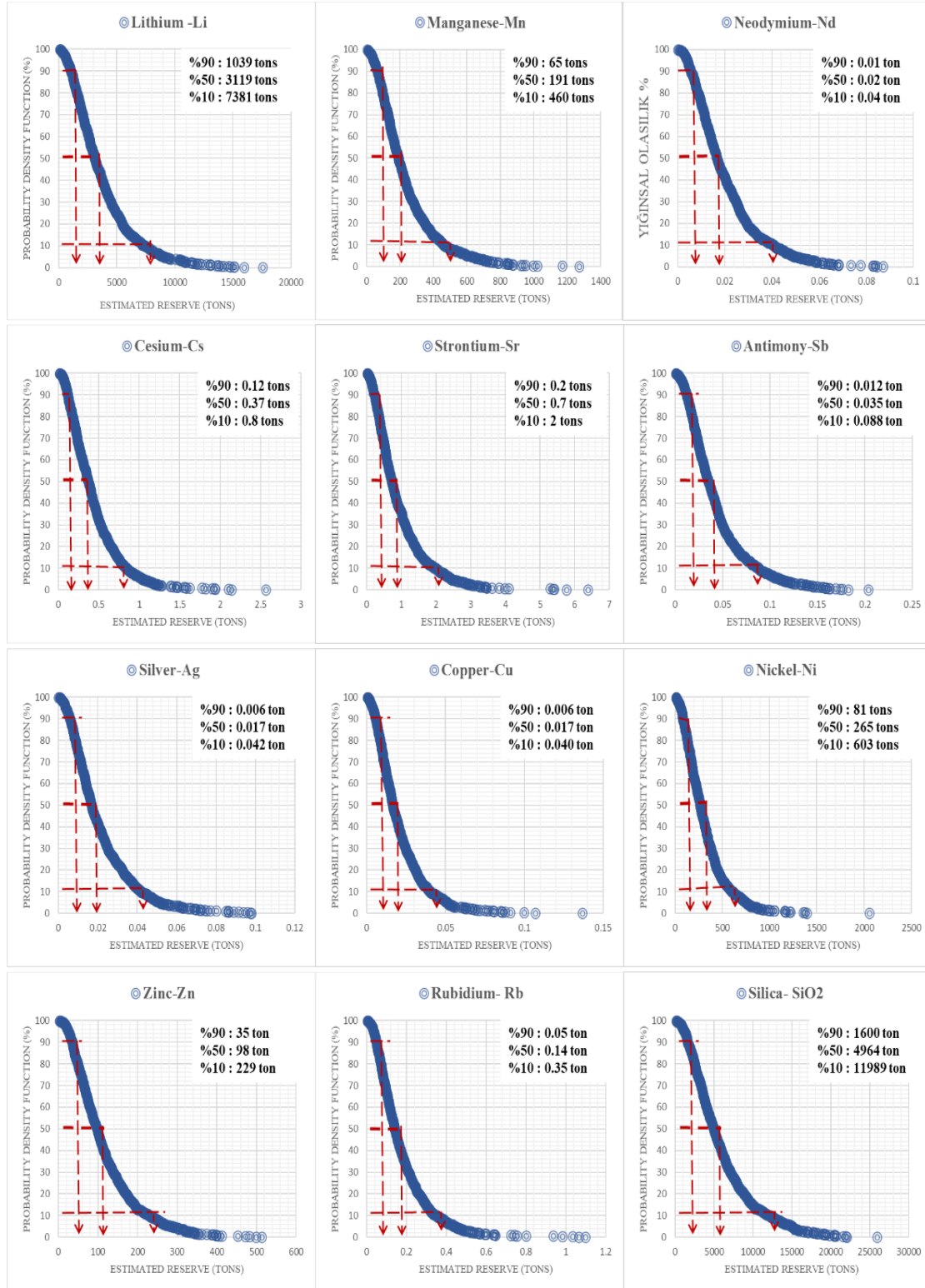


Figure 7: Mineral reserve estimation of Simav geothermal field.

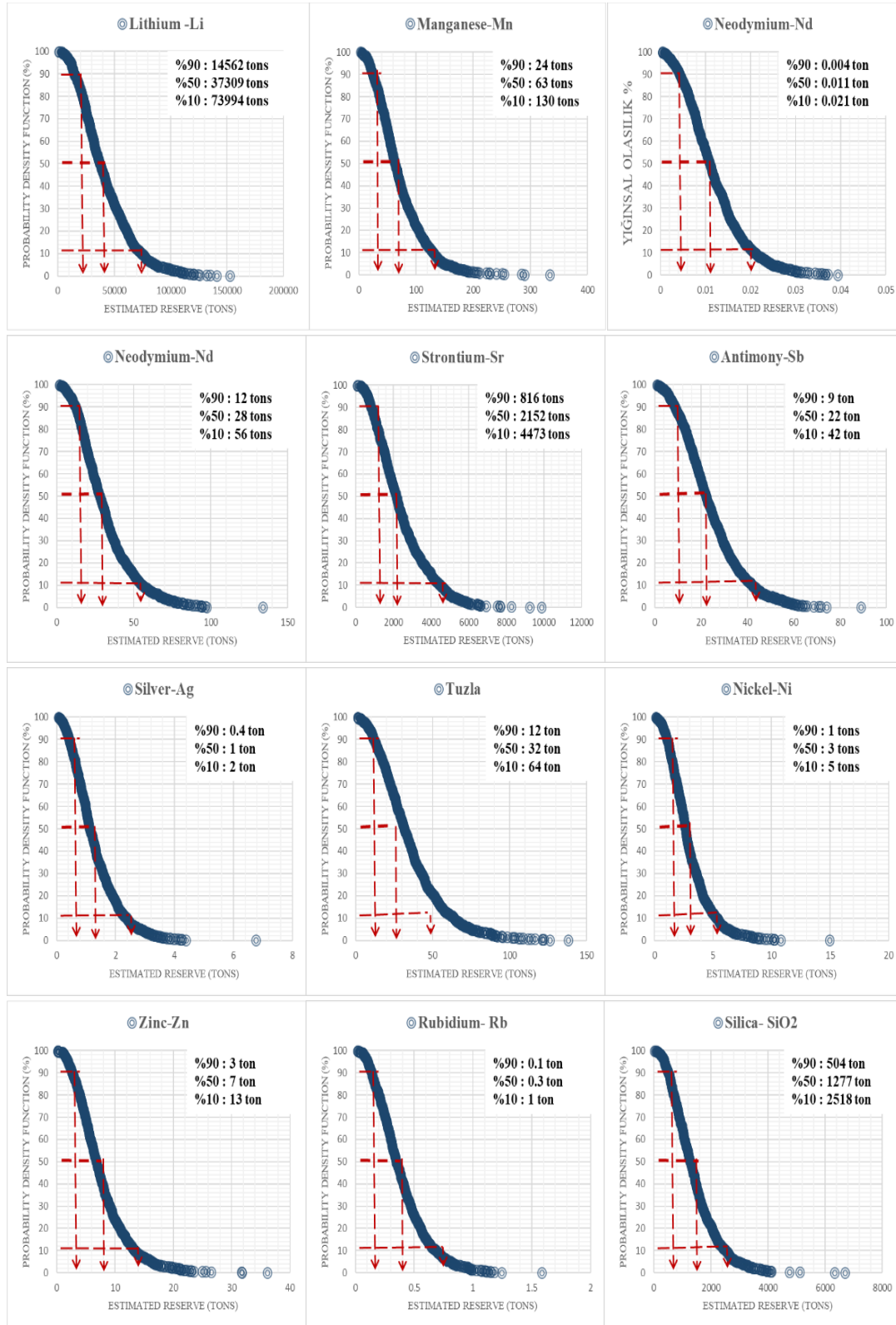


Figure 8: Mineral reserve estimation of Çanakkale Tuzla geothermal field.