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Potential Assessment of Lithium Extraction from Geothermal Reservoirs

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ABSTRACT

Lithium elements in geothermal brine provide tremendous potential for lithium mineral extraction. With recent technological advancements and achievements, lithium extraction from geothermal brine has become a point of interest. Large flow rates from geothermal wells provide a reasonable lithium extraction from geothermal brine. It is essential to delineate the recoverable amount of Lithium from geothermal systems for the economic feasibility of the projects. This study assesses the recoverable lithium mineral potential in geothermal systems using a stochastic approach: Monte Carlo Simulation. One of the productive geothermal reservoirs in Western Anatolia, the Seferihisar geothermal field, is presented as a case study.

1. INTRODUCTION

Lithium is the lightest element among the metals, is generally used as a compound, and is challenging to produce as an ore. It was first described in spodumene, a pegmatite mineral. Lithium pegmatites can be produced from sedimentary (hydrothermally altered clays) and continental salt waters (including geothermal brine) reservoirs. Following pegmatite minerals; spodumene ($LiAlSi_2O_6$), lepidolite ($K_2Li_3Al_4Si_7O_{21}(OH,F)_3$), amblygonite ($LiAl(F,OH)PO_4$) and petalite ($LiAlSi_4O_{10}$) have been used to produce Lithium commercially (MTA, 2017). Khan (2020) presented the global lithium production history and prediction between 2005 and 2025 from brine and rock (Figure 1).

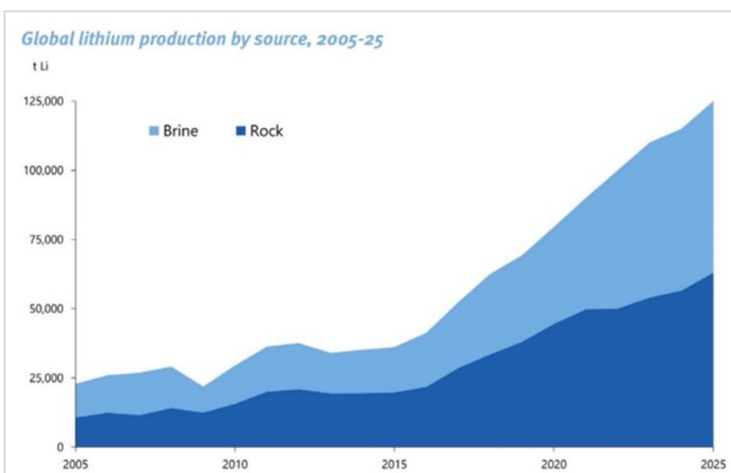

Figure 1: Global lithium production by source prediction for 2005-2025 (Khan, 2020)

Some common features of the formation of lithium-rich brine systems are (1) arid climate; (2) a salt lake; (3) magmatic and/or hydrothermal activity; (4) tectonic subsidence; (5) suitable lithium sources; and (6) sufficient time for Lithium to be enriched in the brine. When lithium enrichment due to hydrothermal activity is examined, it is observed that the hot liquid provides the enrichment of Lithium from rocks, the direct source of Lithium from shallow magmatic brines, and distillation plays a role in Li^+ concentration and contributes to the formation of Li-rich clay mineral (Munk et al., 2016).

Depending on the production of electric vehicles worldwide, battery technologies are also developing. Lithium batteries are also preferred in electric vehicles due to their high power density, long life, relatively fast charging, and lightweight. In parallel with the widespread use of electric vehicles, the world's lithium demand also increases significantly.

The source of the lithium may change around the world, and it causes to study on different mineral extraction methods. In literature, various mineral extraction methods such as ion exchange, solvent extraction, high-capacity membranes (adsorption) proposed by different researchers. Because of the contamination of membrane corrosion effect on pipes, each method has limitations. In this study, we focus on lithium extraction method from brine.

Evaporative concentration is a simple process of obtaining Li. Lithium chloride (LiCl) and lithium carbonate (Li_2CO_3) inorganic compounds can be produced from geothermal brine by evaporative concentration and following refinery processes (Figure 2). Lithium hydroxide mineral is typically produced from refined Li_2CO_3. Reverse osmosis may be used to reach concentrated lithium brine as an alternative to evaporation, and these processes may significantly help to increase the lithium concentration (Stringfellow and Dobson, 2021).

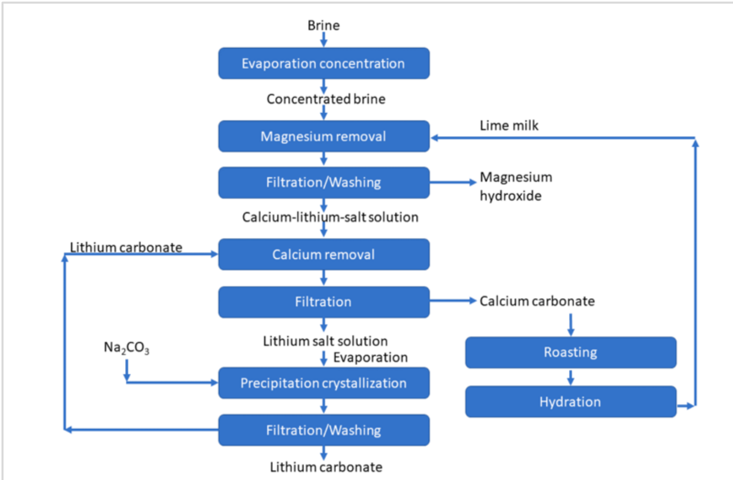

Figure 2: Li_2CO_3 extraction from brine (Meshram et al., 2014)

The classical evaporation process by open ponds looks low-cost operation; however, it requires time and land. It is impossible to reinject this water to the underground to provide reservoir sustainability. This may mean that it is not an appreciated process, especially for geothermal power plants.

The new approach, the direct extraction method, proposes using membranes and electrochemical processes to increase lithium extraction (String fellow and Dobson, 2021). Instead of evaporating all brine and chemically removing all the impurities, this process focuses on extracting the Lithium directly from an unconcentrated brine to produce a lithium eluate, which can be processed to lithium chemicals without evaporation ponds (Grant, 2019). The method uses a highly selective absorbent to extract lithium compounds from the geothermal water. Organic ion-exchange reins, ion-imprinted polymers, inorganic molecular ion-exchange adsorbents (aluminum hydroxides, manganese oxides, and titanium oxides), solvent separations, and membrane separations, electrochemical separation process technologies may use for lithium extraction from geothermal waters.

One new approach is the ion-exchange method for direct extraction of lithium. The technique is used to separate ionic contaminants from the geothermal brine by a physical and chemical process, and impurities are replaced by other ions of the same electrical charge (Figure 3).

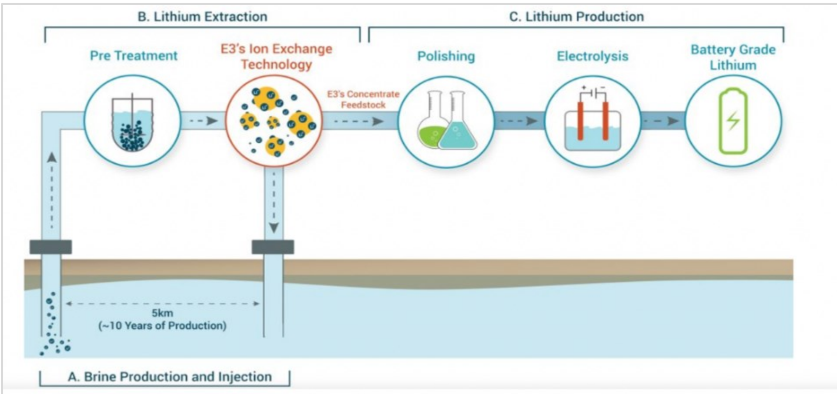

Figure 3: General Overview of Direct Lithium Extraction Ion Exchange Methodology (John, 2018)

Technological advancement of Li extraction from brine is a milestone for utilizing geothermal reservoirs for Li production. Li potential assessment study is a critical part of the feasibility of Li extraction projects. In this study, we investigate the Li potential of geothermal brine by using a Monte Carlo simulation. We present a case study from Seferihisar (İzmir) geothermal field, located in western Turkey.

2. SEFERIHISAR GEOTHERMAL FIELD

There are different geothermal systems in Western Anatolia. In addition to large graben systems such as the Büyük Menderes and Gediz Graben, there are also several geothermal systems close to the Aegean Sea in the region (Tut Haklıdır and Şengün, 2020). Beside electricity production and direct applications, the possibilities of minerals recovery from geothermal brine at these geothermal systems are still being investigated in Western Anatolia (Tut Haklıdır and Şengün, 2019).

Seferihisar geothermal field is located the southwest of Izmir, a province of Turkey. The reservoir fluid is liquid-dominated, and reservoir temperature changes between 70 ºC and 200 ºC, depending on the depth. The geochemical studies for water classification suggested sodium and bicarbonate water types. Li content of geothermal brine and spring water is considerable for the extraction (Table 2).

The field is controlled by Orhanlı Fault Zone, which includes several dextral fault segments extending mainly in a NE–SW-directions from İzmir Bay to Kuşadası Bay (Uzel and Sözbilir 2008) is located in east part of Seferihisar uplift. Tuzla fault has significant effects on the formation and tectonic evolution of the Seferihisar geothermal field (Drahor and Berge, 2006). Various Schist and marble bearing Paleozoic aged Menderes metamorphic and Mesozoic limestones blocks, serpentine and submarine volcanic bearing Flysch formation (Erdoğan 1990) are considered as basement of Çukurdağ Graben, which is located in the northwest of Seferihisar uplift. Graben fill consists of the Miocene aged lacustrine and fluvial Yeniköy Formation at the bottom and the Pliocene-Quaternary aged Cumaovası Volcanics at the top. Rhyolite and rhyodacites contained Cumaovası Volcanics identified as the heat source of the geothermal system, are located in the southeast of the graben as individually presenting domes in Cretaceous formations. Menderes Metamorphic marble, Late Cretaceous limestone, and younger lacustrine limestone constitute the reservoir rock (Eşder and Şimşek, 1975). Magri et al. (2012) presented the hydro-stratigraphic profile of the Seferihisar geothermal area with a vertical exaggeration (Figure 4).

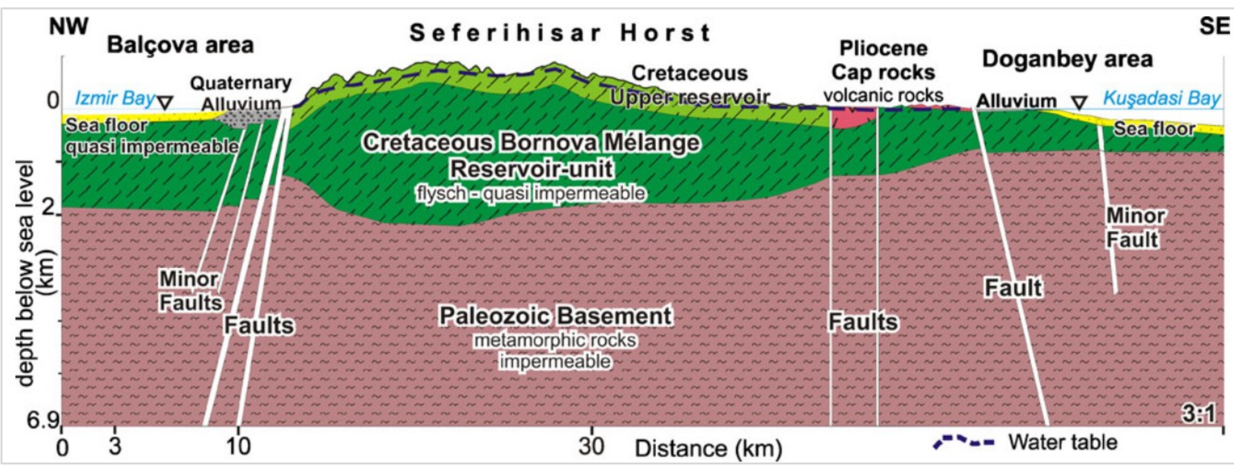

Figure 4: The NW-SE hydro-stratigraphic profile of the study area (Magri et al. 2012)

Table 5: Li concentration of springs and geothermal wells in the Seferihisar geothermal field

Sample Name	Sampling Date	pH	T (°C)	Cond.	B (mg/l)	Li (mg/l)	Reference
Cumalı well	20.06.2016	6.42	-	30100	17.8	13.4	*This study*
Orhanlı well 1	11.06.2020	6.56	27.6	1029	0	0.06	*This study*
Orhanlı well water (cold)	11.06.2020	6.87	24	1032	0	0.1	*This study*
Orhanlı well 3	27.01.2020	8.31	85.9	1029	11	3.44	*This study*
Tuzla Spring	5.11.2020	6.32	91.5	31500	11	10.05	*This study*
Doğanbey Seawater	26.01.2020	8.27	15.6	56000	4.4	0.71	*This study*
Kavadere Dam	26.01.2020	8.34	9.8	410	0.3	0.32	*This study*
Cumalı Spa Spring	03.05.2000	6.25	66	30200	16.6	12.23	*Tarcan and Gemici, 2003*
G-2 well		7.50	137		12	10.8	*Yılmazer, 1984*
G-7 well		6.89	86		22	9.87	*Yılmazer, 1984*
Karakoç Spa Spring	03.05.2000	6.54	59	7400	9.3	4.14	*Tarcan and Gemici, 2003*

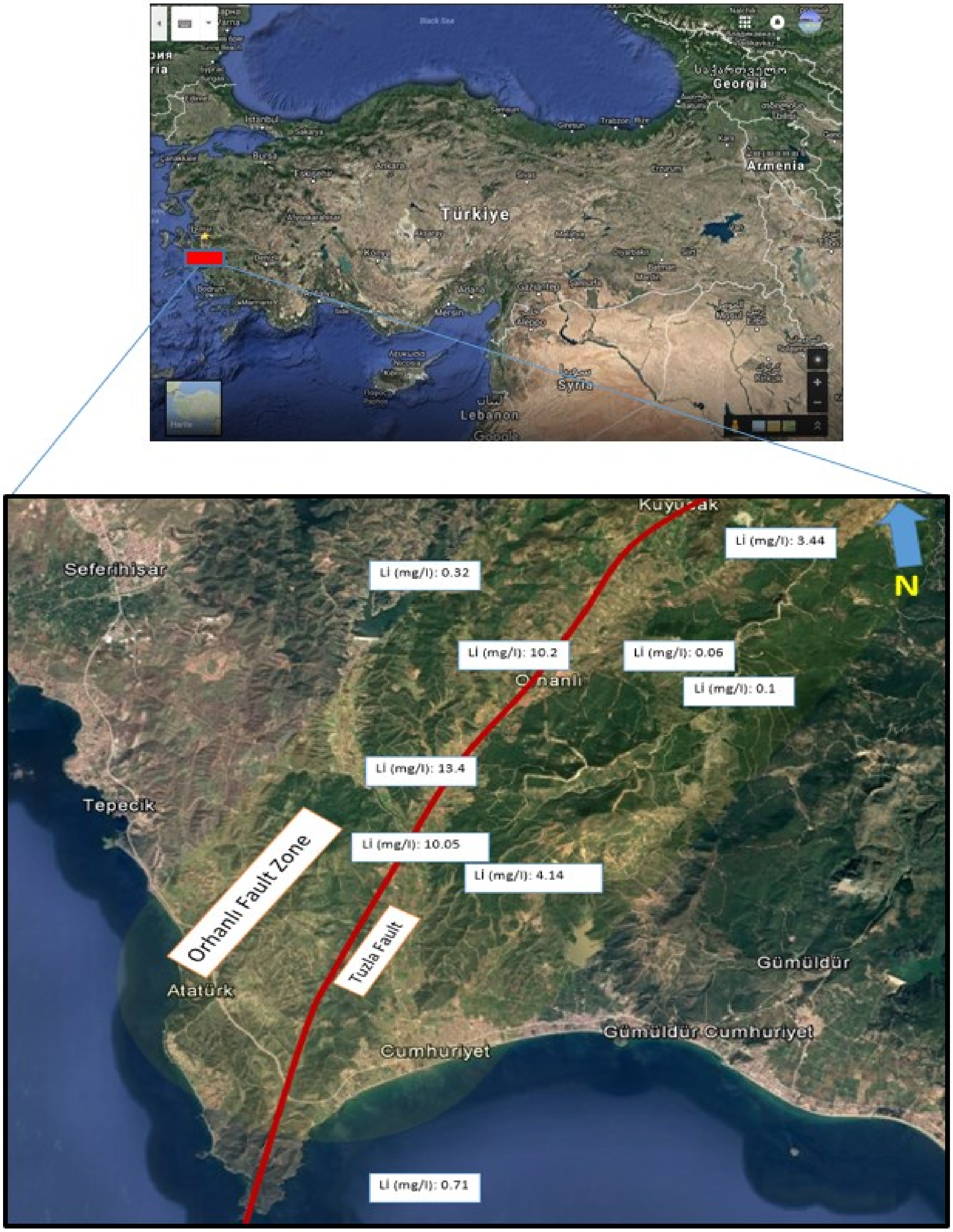

Figure 5: Distribution of Li concentration in Seferihisar geothermal field

3. METHODOLOGY

The potential of Li in the Seferihisar geothermal field was assessed by using a volumetric reserve estimation method introduced by the U.S. Geological Survey, which is typically used to estimate geothermal energy potential. Muffle (1978) modified the volumetric method with a probabilistic approach called Monte Carlo simulation to account for uncertain reservoir parameters such as area and thickness. We adapted this approach to estimate the Li potential of geothermal systems. The volumetric method is based on a volumetric calculation of Li in the geothermal brine occupying rock porosity and fracture media. The Li potential in the rock grain was ignored, and Li transfer from rock grains to brine due to concentration difference was assumed negligible during production from the geothermal reservoir.

$$\text{Recoverable Li mass} = A*h*\Theta*C*RF*E \tag{1}$$

where, "A": reservoir area (km^2); "h": reservoir thickness (m); "Θ": equivalent porosity (fraction); C: Li concentration in brine (ppm); RF: Recovery Factor (fraction); E: Extraction efficiency

Equation 1 refers to the recoverable Li amount in the geothermal brine found in the pore space of geothermal reservoirs. There is significant uncertainty in the calculation of reserve estimation. All the parameters used in equation 1 include uncertainty due to heterogonous geothermal reservoirs. It is difficult to determine the most likely value of the parameters. Therefore, the probabilistic approach might address the uncertainty by providing the probabilistic occurrences of results. Monte Carlo simulation is a widely used stochastic method for reserve estimation.

The Monte Carlo method provides a mathematical model that includes a dependent variable as a function of independent variables. It relies on the probabilistic distribution of each parameter and provides an estimation by including all uncertainties in the variables. The dependent variable is Li mass, and independent variables are reservoir area, thickness, porosity, Li concentration, and recovery factor. The important distribution functions used for uncertainty in Monte Carlo simulation are normal distribution, lognormal distribution, and triangular distribution. In this study, we performed a Monte Carlo simulation in an Excel-based spreadsheet. We used the triangular distribution function due to a lack of data. The triangular distribution is useful when the size of data is limited. In the triangular distribution, minimum, maximum, and most likely values are used to create the probability density function in a triangular fashion (Equation 2, 3, and 4). Hence, many dependent variable values are found with the different values of independent variables.

$$x = \frac{2*(x-a)}{(b-a)*(c-a)} \quad \text{for } a \le x < c \tag{2}$$

$$x = \frac{2}{(b-a)} \quad \text{for } x = c \tag{3}$$

$$x = \frac{2*(b-x)}{(b-a)*(b-c)} \quad \text{for } c < x \le b \tag{4}$$

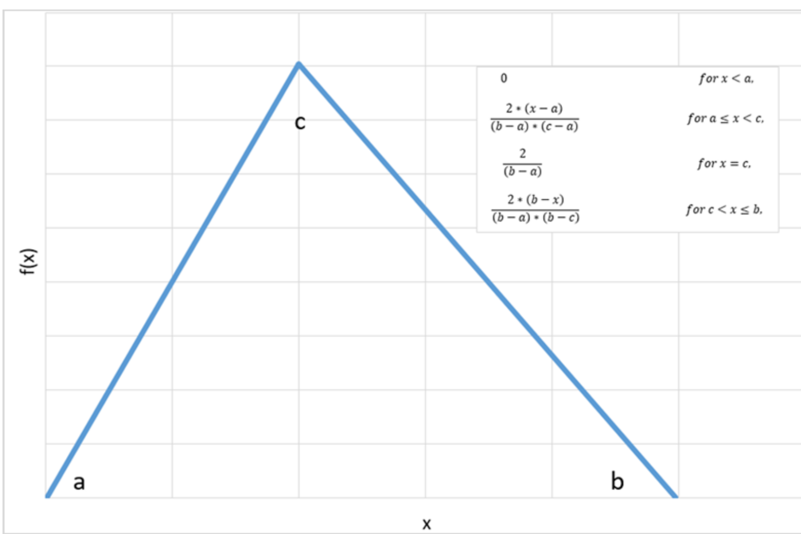

Figure 6: The triangular distribution function and graph (Aydin and Merey, 2021)

The values of input parameters used in the calculations are given in Table 1. The reservoir area is defined using previous geochemical, geological, and geophysical studies available in the literature. Magri et al. (2012) reported the reservoir thickness varying between a few hundred meters to more than 2 km in the region. In the reservoir simulations of fields in western Turkey, the porosity value of metamorphic rocks was assumed to be less than 10 % (Aydın and Akın, 2020; Küçük, 2018). Li concentration of geothermal brine changes between 0.7 ppm and 15 ppm in the study area. The recovery factor of geothermal reservoirs is a controversial subject. The investigators mostly focused on the energy recovery from the reservoir. The reported recovery factors change between 5 % and 24 % based on the porosity and permeability of the systems (Williams et al., 2008; Avsar et al., 2015). Li extraction efficiency from geothermal brine depends on the implemented technique. Sun et al. (2020) proposed a green recovery of Li based on the iron phosphate electrochemical technique. The extraction efficiency was reported as 90.65 % as the maximum value. Harrison (2014) reported Li extraction efficiency greater than 95 % at the laboratory scale experiments using sorbents. Mceachern et al. (2020) obtained an extraction efficiency of less than % 60 with aluminate-based adsorbents.

Table 1: Input parameters for Monte Carlo simulation

	Minimum	Mean	Maximum
Area, km^2	20	25	30
Thickness, m	500	1000	1500
Porosity, %	3	5	10
Concentration, ppm	0.7	10	15
Recovery Factor, %	10	15	20
Extraction Efficiency, %	50	70	90

4. RESULTS AND DISCUSSIONS

This study investigated the Lithium potential of the Seferihisar geothermal field with a volumetric method. The field shows heterogeneous behavior in terms of reservoir parameters and Li concentration. A spreadsheet-based Monte Carlo simulation was performed to account for uncertain parameters. Distribution functions of input parameters are typically used to handle the variation of the dataset. The most widely used distributions are lognormal, normal, and triangular distributions. In practice, a large dataset of input parameters is matched with distribution functions to use appropriate distribution in the Monte Carlo simulation. Due to lack of data, we utilized triangular distribution, which is useful for limited data. Monte Carlo simulation results are shown in Figure 7. The proved Li reserve of the Seferihisar geothermal reservoir is estimated as 583 tons. The probable and possible Li reserves are 1269 and 2325 tons, respectively.

In the studied area, the contribution of seawater with almost zero Li concentration to the geothermal reservoir is significant. Therefore, there is a risk of a sharp decline of Li concentration after some production time. The Li extraction method has a tremendous effect on the recoverable Li amount. The highest efficiency of the extraction method might not be cost-effective. Therefore, performing a feasibility study before a given decision is essential.

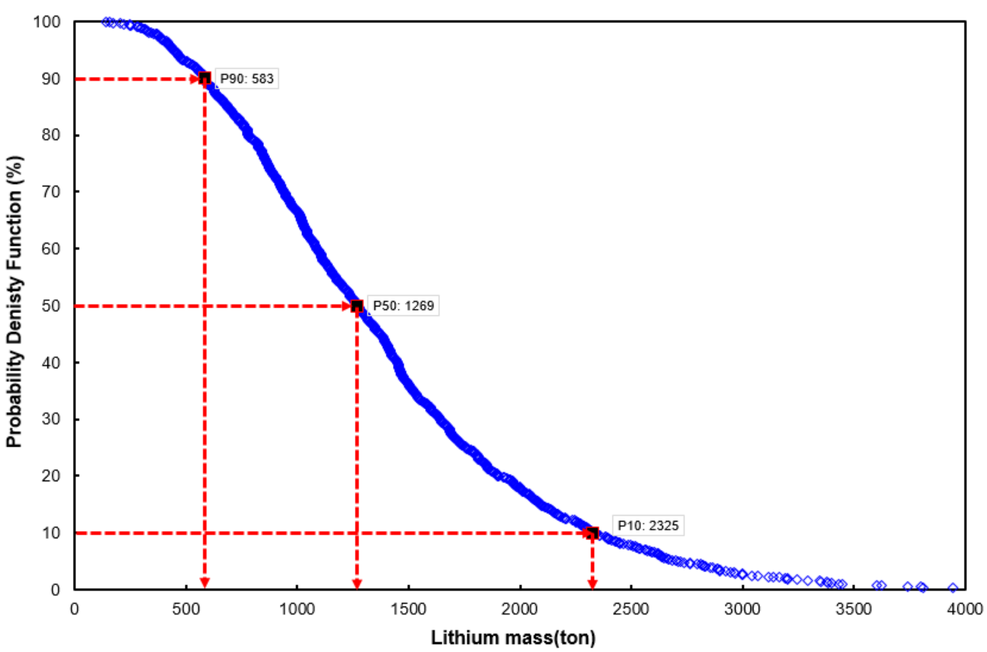

Figure 7: Potential of Lithium mass in Seferihisar geothermal reservoir

5. CONCLUSION

The tremendous potential of Li in geothermal brine might meet the increasing demand of the Li market in the next decade. The technological advancements in the Li extraction from brine are a milestone for utilizing geothermal reservoirs as a Li source. This study estimated the Li potential of a productive geothermal reservoir in western Anatolia, the Seferihisar geothermal field. The field geological and geophysical structure are reviewed from the previous studies. Li concentrations of existing wells and springs in the field are collected and measured. We used a volumetric method to assess the reservoir's Li potential. The Monte Carlo simulation was performed to decrease the uncertainty of the input parameters. Due to lack of data, we utilized triangular distribution for all uncertain parameters. The simulation results showed that the proved Li reserve of the Seferihisar geothermal reservoir was estimated as 583 tons. The probable and possible Li reserves are 1269 and 2325 tons, respectively. The field observations suggested that seawater strongly supports the geothermal reservoir, which is favorable for the sustainability of the resource. However, it is not desired from the point of Li recovery since the seawater has a lower Li concentration than the geothermal brine in the field. This means that, there is a risk of a sharp decline in the Li concentration as the Seferihisar field puts on the operation.

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