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Lithium Extraction Potential from Costa Rican Geothermal Field Brines

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ABSTRACT

In Costa Rica, there are two high enthalpy geothermal fields: "Las Pailas" (LP) and "Alfredo Mainieri Protti (AMP)", both characterized by its high brine content (around 75%) and exploited to generate electricity. LP reinjects 410 l/s of brine, while AMP reinjects 1000 l/s of brine, in a continuous basis.

The main objective of this work consisted of determining the lithium extraction and exploitation potential from different geothermal brines, to use it later as raw material in manufacturing electrochemical batteries. Lithium contained in brines was quantified and extraction processes were determined in order to select an optimal option to implement.

Initially, brine species were quantified including lithium, silica, boron, arsenic, iron, sodium, potassium, calcium, phosphorus, sulfates, sulfur, chlorine, among others through the following methods: i) inductively coupled plasma mass spectrometry (ICP-MS), ii) inductively coupled plasma optical emission spectrometry (ICP-OES), iii) ion chromatography, iv) alkaline titration to determine inorganic dissolved carbon and v) X-ray fluorescence (XRF). Measured Li concentration was obtained as 10 mg/kg for AMP's reinjection brine and 18 mg/kg for "Las Pailas" reinjection brine. This represents a gross potential of 521.8 ton per year of lithium when adding both geothermal fields.

Additionally, an extensive bibliographic review about lithium extraction processes was carried, different methods were found and grouped according to the following types: i) co-precipitation, ii) adsorption and ionic exchange, iii) solvent extraction and iv) electrochemical techniques, this last group was selected to comply with the restriction of extracting the lithium without affecting the normal flow of the brines. Specifically, electrodialysis was selected as the method to test lithium extraction in a controlled environment, since electricity in Costa Rica is around 99% from renewable sources, and this process would extract materials in a sustainable manner. Under laboratory conditions, a first electrodialysis cell was built, by applying the method with Las Pailas and AMP brines, lithium concentration increased 36% in the best case.

1. INTRODUCTION

Lithium-ion electrochemical batteries offer great advantages for massive energy storage, this technology is growing in the market due to its energy density, specific energy, charge capacity, fast discharge, and long-lasting life cycle compared to other like alkaline and acid lead batteries (Díaz-González, Sumper, Gomis-Bellmut & Villafáfila-Robles, 2012). Lithium is mainly used to manufacture electrodes mostly from lithium carbonate, demand of this salt is projected to increase in the following years. Global demand from 2019 to 2030 is expected to grow 1,3 million tons, according to Jones, Acuña & Rodríguez (2021).

Different extraction techniques have been developed to isolate lithium carbonate species from fields and deposits, some of them highly efficient and cost-effective, these techniques include co-precipitation, solvent extraction, adsorption and ionic exchange, and some electrochemical techniques. The latter requires less time pretreating the brines compared to other processes as co-precipitation or solvent extraction. Many researchers suggest non-lithium-selective chemical substances while applying adsorption or solvent extraction, these methods require further chemical processing to obtain a lithium product that is useful to build batteries. Electrochemical processes require fewer polluting substances, and require a smaller area to be deployed, for example in co-precipitation large salt ponds are used to evaporate and obtain lithium carbonate.

59% of global lithium extraction utilizes co-precipitation from salt deposits, and the main continental deposits are located between Bolivia, Argentina, and Chile (Meng, Mcneice, Zadeh & Ghahreman, 2019). Brines also have sodium, calcium, potassium, chlorine, silica, sulphates, and bicarbonates, analysis of these brines show lithium presence in smaller quantities, but enough to extract it from a concentrated brine.

Although many continental brines have more than 100 mg/kg of lithium that are considered suitable for extraction, in Costa Rica geothermal brines show reduced contents of lithium between 3 mg/kg to 9 mg/kg. There are two main fields, the first, Geothermal Field Alfredo Mainieri Protti (AMP) located in Bagaces, Guanacaste has a brine flow of 1000 L/s with enthalpy of 980 kJ/kg – 1150 kJ/kg, the second Geothermal Field Las Pailas (LP) located near Rincón de la Vieja Volcano has a brine flow of 410 L/s with enthalpy of 979 kJ/kg – 1251 kJ/kg (Instituto Costarricense de Electricidad, 2015).

2. METHODOLY AND RESULTS

2.1 Geothermal fields samples characterization

Samples from reinjection brines were taken from LP and AMP geothermal fields, potentiometric parameters were determined and chemical species were quantified though different techniques (ICP-MS, ICP-OES, ion chromatography, alkaline titration and XRF). This quantification was carried to understand concentration of species that are commonly present in brines and are normally higher than lithium, for example sodium, chlorine, and potassium, this presence can involve brine pretreatment stages to obtain enough lithium concentration.

Potentiometric parameters as temperature, pH and conductivity were measured on site at each geothermal field, Table 1 shows measured parameters. From the geology perspective, many aspects can impact the measurements: geological structures, rock types, well topography and weather (Arnórsson, Bjarnason, Giroud, Gunnarsson, & Stefánsson, 2006).

Table 1: Potentiometric parameters of LP and AMP reinjection brine samples.

Parameter	Las Pailas (LP)	Alfredo Mainieri Protti (AMP)
Temperature [°C]	136	136
Pressure [bar]	5.5 – 5.8	5.5 – 5.8
Conductivity [µS/cm]	18680	11500
Density [kg/m^3]	1009	1009
pH [-]	7,59	7,65

Many dissolved compounds and minerals solubility are pH dependent, this means that relative species depend on the fluid's pH level, for example hydrolyzed cations, weak acids, or bases. Exposure of brine to atmosphere could also affect the CO_2 dissolved concentration (Arnórsson et al., 2006). PH shown in the samples is near neutrality, this level needs to be sustained to avoid damages in the equipment, in some cases caustic soda is used to maintain pH around 7. At the same time, pH is temperature dependent due to the constant acids and bases dissociations. Measured temperature in the geothermal fields varies from 136 °C to 165 °C. Due to the high contents of silica in the brines, precipitation of this compound increases when temperature decreases. This should be considered in the equipment treating the brine and extracting the lithium, if temperature is decreased silica precipitation in pipes is expected and efficiency can be compromised.

High conductivity values imply high quantity of dissolved ions in the brine, the range observed in the samples is between 11500 µS/cm and 18680 µS/cm. This means that extraction processes of specific lithium salts can lead to more complex stages to reduce impurities. LP shows higher conductivity values than AMP.

High pressures in the geothermal processes of AMP and LP (around 5.5 bar) suggest the need to maintain this condition in a treatment plant to extract lithium, these values should not be modified preferably, since lower pressures can lead to higher levels of vapor and subsequent stages that can involve higher deployment costs.

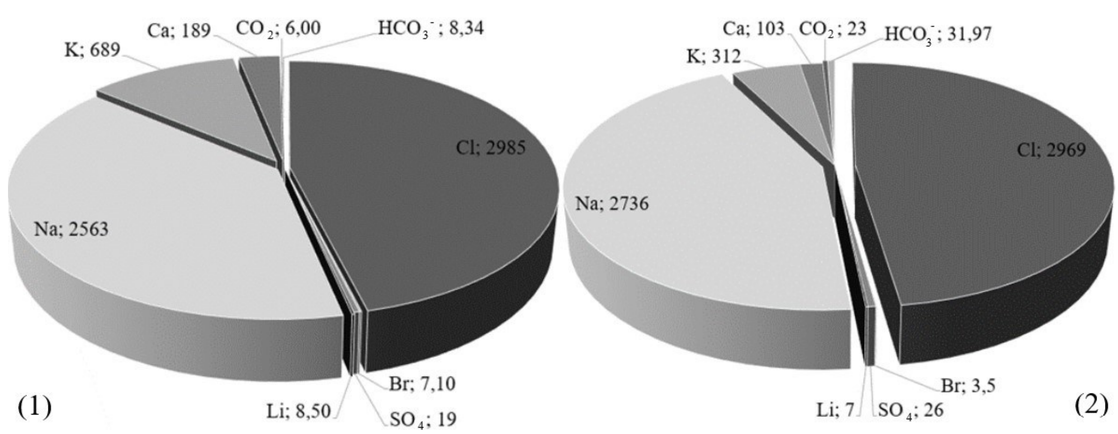

Figure 1: Sample composition in mg/kg of different geothermal injection brines from (1) LP and (2) AMP.

Species quantification was carried through ion chromatography (IC), this technique determines the different ionic components from a sample using selective ionic exchange with a column that contains counter anions in a stationary phase (Mayolo-Deloisa, Martínez, &

Rito-Palomares, 2012). This analysis filters the samples with a cellulose acetate membrane that contains porous from 0.2 µm to 0.45 µm, sample storage is carried in high density polyethylene or polypropylene bottles. Figure 1 shows composition found in the samples.

Even though lithium quantity is low with respect to other species in the brine, the concentration found indicates the possibility of lithium extraction, as long as concentration increases and impurities not related to lithium extraction are removed. Studied brines are rich in Na^+, K^+, Ca^{+2} and Cl^-, this implies that the selected extraction method should be extremely selective to cations with specific size, since Li^+ compared to other species has a much smaller particle size.

When brine temperature changes composition is the same, but speciation can be modified. Different operation conditions were modeled through simulation in PHREEQC software, simulations showed the type of lithium salt that can be obtained from the geothermal process when applying different extraction techniques, and the most common phase of lithium found in the brine.

Table 2. Lithium composition percentage in analyzed brines from LP and AMP through simulation in PHREEQC, with geothermal plant conditions.

Species	Las Pailas [%]	Alfredo Mainieri Protti [%]
Free cation (Li^+)	99,81	99,68
Lithium chloride (LiCl)	0,16	0,29
Lithium sulfate ($LiSO_4$)	0,03	0,03
Lithium bromide (LiBr)	0,01	0,00
Lithium hydroxide (LiOH)	0,00	0,00

The most common species of lithium is found as a free cation, this will enable an extraction process without the need of using a complex salt. These ions can react with ions like chlorine, that is highly concentrated in the brine. Lithium chloride is expected to be the predominant salt to be formed in an extraction plant.

2.2 Electrodialysis to increase concentration

As a first stage to be deployed in a lithium extraction plant in series with a geothermal power plant, a concentration stage is suggested. This stage should use conventional electrodialysis, using approaches like the one indicated by Jiang, Wang, Wang, Feng, and Xu (2014). Electrodialysis is a process that consists of ion transportation through selective membranes under the influence of an electric field, which provides the energy to move and separate ions or charged molecules. Ions are transferred from a substance less concentrated to a substance more concentrated (Tanaka, 2015).

Electrodialysis cells work attracting cations to a negative electrode (cathode), where a reduction reaction takes place, while anions will be attracted to the positive electrode (anode), where an oxidation reaction takes occurs. These electrodes are conductor materials that permit the current flow; besides they are built with neutral materials to avoid degradation (Seader, Henley & Roper, 2016). Cationic and anionic membranes alternate, creating compartments of concentrate solutions. Membranes should be resistant to wide pH changes (between 1 to 10) from an electrical and chemical perspective, this will assure longer life and cycles.

Electrodialysis cell was filled with geothermal brine. A scale model was built with three anionic and three cationic membranes, creating four compartments of brine, two of them will concentrate lithium ions. Stainless steel electrodes were used, and their compartments were protected with a Na_2SO_4 electrolyte, this avoids oxygen and chlorine gas formation. The total cell volume was 2.3 L, built with acrylic walls and separator, figure 2 shows a picture and a diagram of the system built.

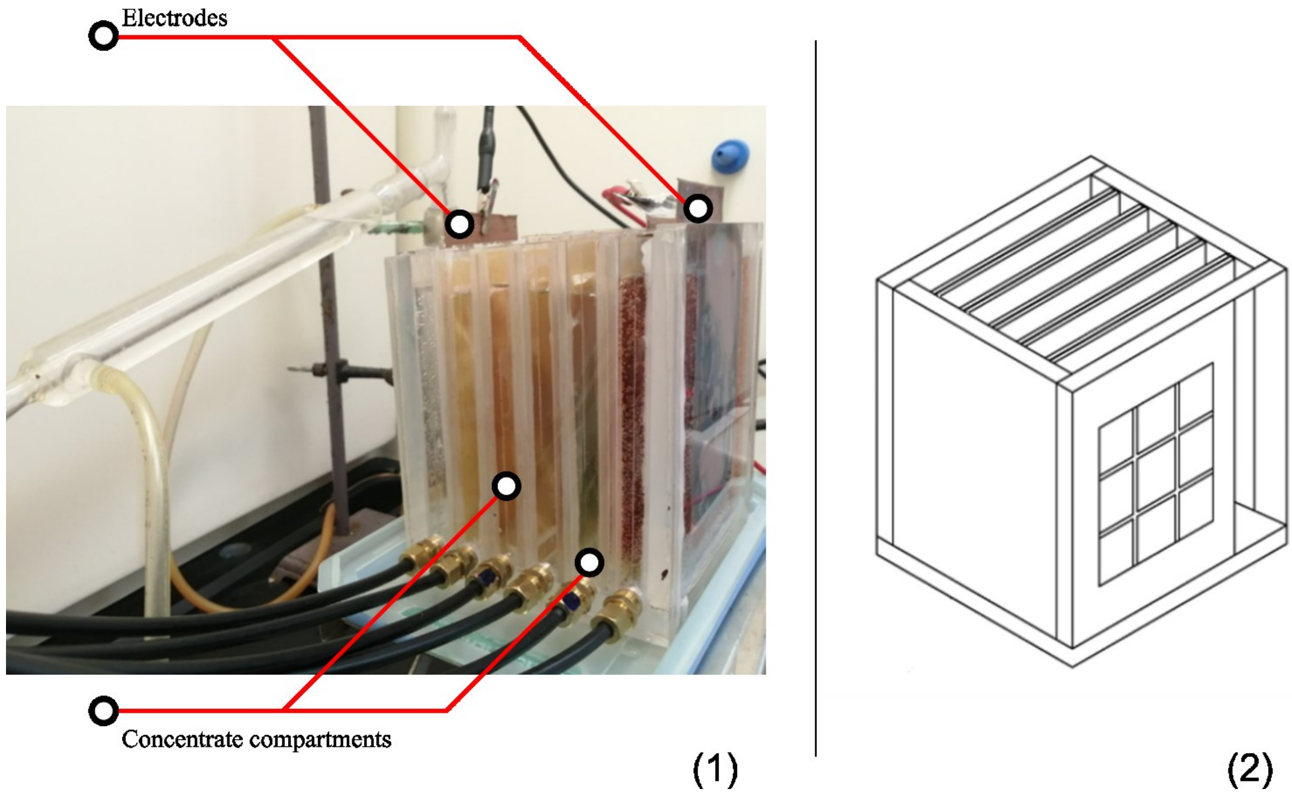

Figure 2: Electrodialysis cell built to concentrate lithium (1) picture of the system and (2) schematic of the acrylic walls and separators.

The membranes used in this first cell were CMI-700S as cationic membrane and AMI-7001S as anionic membrane, they are manufactured from polystyrene gel with interlaced divinylbenzene, and a functional group of quaternary ammonium (anionic membrane) and sulfonic acid (cationic membrane). The prototype cell was used to concentrate lithium and other species, voltage was fixed to 15 V, while current between electrodes started at 1.5 A and 2.3 A, and the process was stopped until current was reduced around 0.2 A - 0.5 A, according to the records of a referenced research (Jiang et al., 2014). Figure 3 shows how the electrical current changes in time, and it is reduced as the concentrate level increases. Since two compartments reduce ionic concentration, higher resistance is expected to be obtained and a reduction of the electrical current (Jiang et al., 2014).

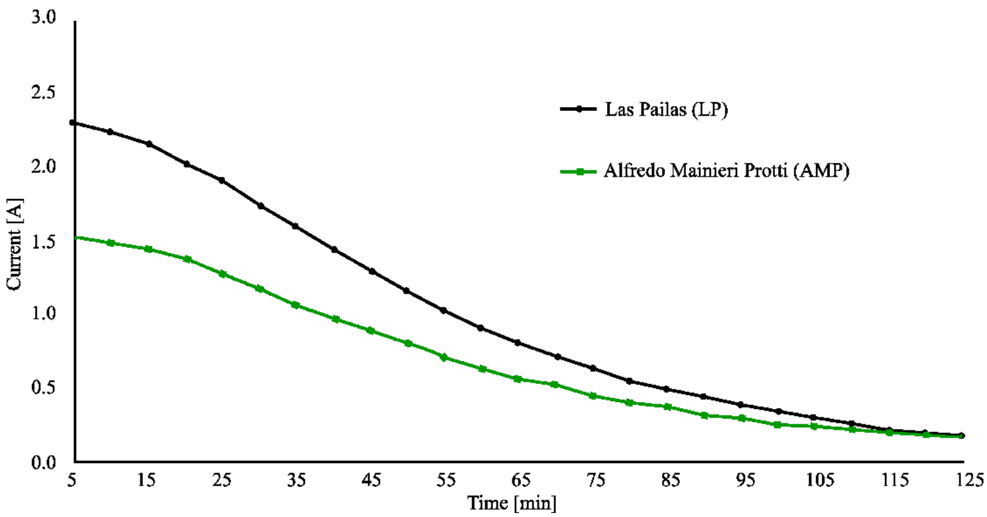

Figure 3: Change of current in time while concentrating solutions from LP and AMP reinjection brines.

Las Pailas geothermal reinjection brine shows higher concentrations of species (sodium, potassium, calcium, and chlorine), this means that more ions will be dissolved when applying electrodialysis and more energy is consumed transporting the ions. Energy consumption was obtained for both sampled brines, LP required 85 Wh and AMP required 90 Wh to saturate within 2 hours of running the electrodialysis process.

After electrodialysis stage, a result of 185 mL of concentrated brine was obtained for both geothermal field samples. Quantitative analysis through ion chromatography and alkaline titration were conducted to determine the final concentration of species. All species, except calcium, increased in concentrated brines, figure 4 shows percentual variation of the species for each sampled brine.

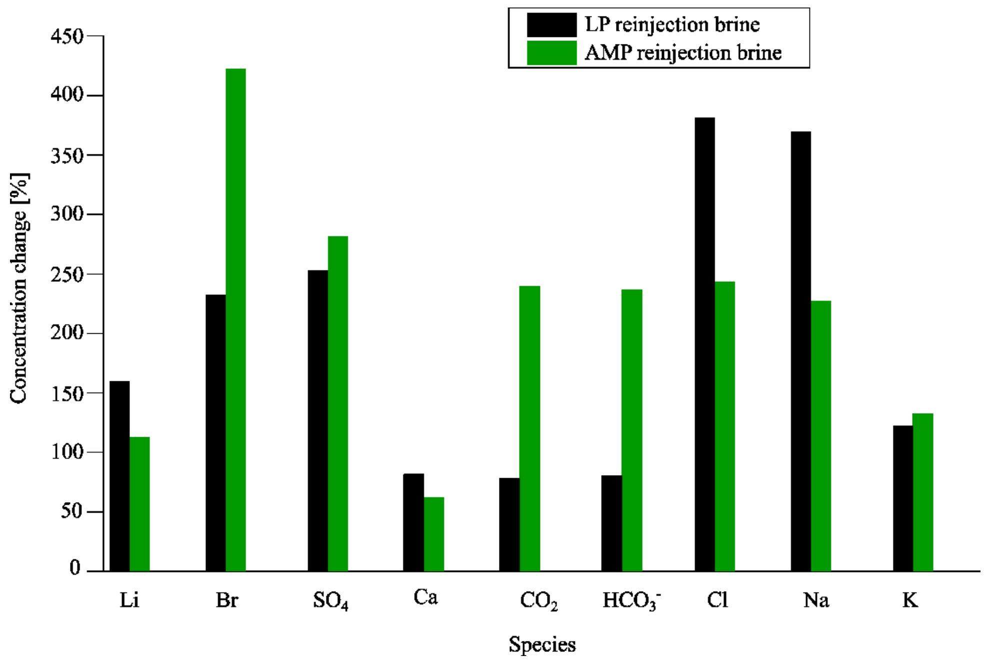

Figure 4: Percentage variation of species after applying an electrodialysis stage to LP and AMP reinjection brines.

Table 3 shows lithium concentration change comparing the original and concentrated samples, findings suggest that just one simple electrodialysis stage is not enough to capture acceptable levels of lithium concentration, that will allow extraction in a feasible manner. This indicates several series of electrodialysis stages will be necessary to obtain higher lithium concentration.

Table 3. Lithium concentration in mg/kg measured from original and concentrated brines from LP and AMP geothermal field reinjection outlet.

Sample	Original concentration [mg/kg]	Post electrodialysis concentration [mg/kg]
Las Pailas (LP)	8.50	13.50
Alfredo Mainieri Protti (AMP)	7.00	7.83

The marked difference between concentration achieved through the same electrodialysis process, is due to a higher starting level of lithium, and the cleanness of the membranes could affect the process performance.

2.3 Lithium extraction plant proposal

The objective of the laboratory tests was to understand steady and controlled conditions, also, to propose a second phase scale model plant but this time with real pressure and temperature conditions from the geothermal power plant, through simulation several parameters were determined. According to Mroczek, Dedual, Graham & Bacon (2015) preheating the brine before lithium extraction is recommended to reduce the energy that the system requires to transport ions to the concentrate, for that reason brine temperature should not be below 60 °C at the reinjection section of the geothermal plant, where the electrodialysis process will run. Brine will reach membranes through divided pipes as a serial system within the geothermal power plant, once membranes are reached lithium ions will be transported to a concentrate, but brine will continue its normal flow back to the plant and the heat deposits.

After first extraction stage, cascade electrodialysis processes are proposed to reach a higher lithium concentration, for industrial applications like this, cells most contain between 100 and 600 membranes and hundreds of concentrate compartments with similar distances that the ones tested in laboratory (0.5 mm to 2.0 mm), area of each membrane should be between 0.4 m^2 and 1.5 m^2 (Seader et al., 2010). Diluates should be restored back to the reinjection well.

After electrodialysis, chemical treatment is necessary to extract a final lithium product from a lithium chloride, these species are the ones expected to mainly prevail, according to PHREEQC simulations. Proposed treatment consists of carbonation of the concentrate to transform the salt to lithium carbonate, this latter is used in the manufacture of lithium batteries. Carbonation uses Na_2CO_3 in a reactor at minimum temperature of 90 °C, lithium salt precipitate expected is Li_2CO_3 (Harrison, 2012). Figure 5 show a block diagram with the proposed process for both geothermal power plants in Costa Rica.

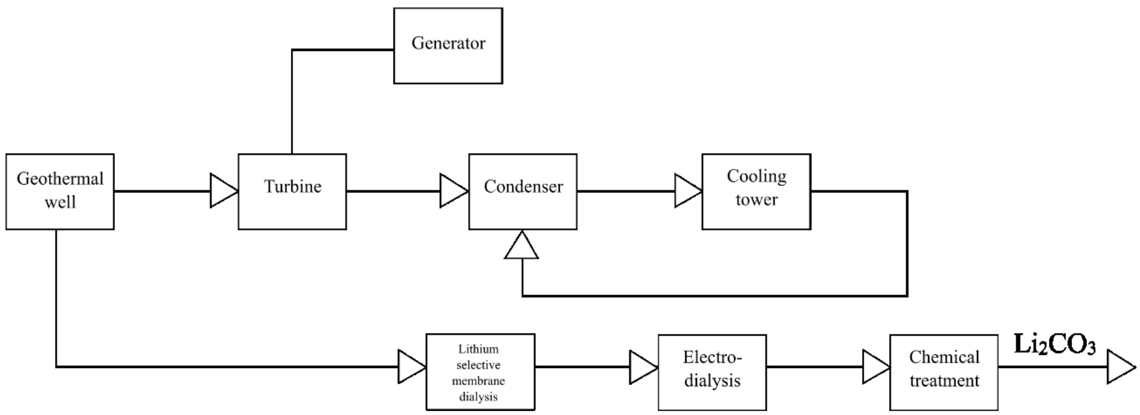

Figure 5: Block diagram showing the proposed process to extract lithium salts from LP and AMP geothermal fields.

3. CONCLUSIONS

Las Pailas geothermal field has a higher natural concentration of lithium in its injection brine compared with Alfredo Mainieri Protti geothermal field. Both sampled brines are rich in ions like sodium, potassium, calcium, and chlorine. To extract lithium, methods like co-precipitation or solvent extraction can be implemented, however an electrochemical process was selected due to its numerous advantages since it can be deployed in series with the geothermal power plant, besides no other chemical substances need to be applied necessarily.

After a first cell deployment for electrodialysis testing, both brines were successfully concentrated in its lithium contents, other species also increased concentration. Later simulations supported a proposal for a second extraction scale model plant, this is the following step looking forward to deploying a serial process for lithium extraction in Costa Rican geothermal power plants. PHREEQC showed that the most likely species to be found in the solution is lithium as a free cation, under the operational pressures and temperatures of the plant.

Table 4 shows theoretical calculations of the amount of lithium that is present in the geothermal brines, this technical potential gives a guidance about the quantities that an extraction plant could aim to exploit in the geothermal fields.

Table 4. Technical potential for lithium extraction of LP and AMP geothermal fields.

Parameter	Las Pailas (LP)	Alfredo Mainieri Protti (AMP)
Brine flow [L/s]	410	1000
Lithium technical potencial [ton/year]	238	284
Lithium salt (CLE[1]) technical potential [ton/year]	2808	3348
Energy storage technical potential using the CLE[1] as raw material [MWh/year]	1872	2232

[1]CLE refers to lithium carbonate salt.

As shown in figure 5, it is recommended to implement a dialysis stage before electrodialysis, using polymeric lithium-selective membranes, to avoid other species or impurities that could reduce the efficiency of the system. Life cycle of these membranes should be monitored and washing processes should be implemented to improve extraction rates.

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