

Lithium Extraction from Wairakei Geothermal Fluid using Electrodialysis

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ABSTRACT

Fluid sourced from the Wairakei geothermal power station was treated at small laboratory scale by electrodialysis. The fluid was first desilicated using electrocoagulation with aluminium electrodes. The influence that the voltage, current, fluid temperature, and acidification had on lithium extraction was explored. It was determined that the power supplied to the system determined the extraction rate while also severely degrading the membranes. Acid dosing was found to be essential to the electrodialysis process due to the alkalinity of geothermal desilicated brine. The greatest extraction rates were obtained at a pH of about 2-4, and the highest extraction rate achieved was 0.28 mg/hour.cm² of active membrane using a three membrane stack in the laboratory electrodialysis unit. It was determined that the process had sufficient potential to be taken into the pilot plant stage which would produce an understanding of the economic viability.

1. INTRODUCTION

The economic viability and the future prospects of mineral extraction from geothermal brines, especially lithium, were recognized by Kennedy as early as 1957 at the commencement of production from the Wairakei Field (Kennedy; 1957; 1961). However it is only in recent times that increasing demand has spurred interest in recovery of lithium from non-traditional sources. Lithium is a valuable metal (~ \$US5000/tonne lithium carbonate) as it has a number of desirable characteristics and uses. The expected annual growth rate between 2011 and 2025 from existing market applications is 7%, with an annual maximum rate as high as 10%, depending on the demand of the electronic and transportation sectors (Roskill, 2009).

This study investigated the potential for extraction of lithium by electrodialysis from the brines at the Wairakei Geothermal Field. Wairakei fluids have a high lithium/magnesium ratio, and the concentration of lithium of ~ 13 mg/L is high compared to other New Zealand geothermal fields, while the silica concentration is low (600-700 mg/L). These characteristics are beneficial for the extraction process; in particular, lower silica concentrations may decrease pre-treatment costs. Treatment costs are further decreased by the low buffering capacity of the fluid, decreasing the amount of acid required to lower the pH.

2. ELECTRODIALYSIS

2.1 Introduction

The electrodialysis system is comprised of alternating anion and cation specific membranes and three fluid streams, diluate, concentrate and catholyte and anolyte electrolyte (Figure 1). The diluate stream contains the source of lithium to be extracted, the concentrate becomes enriched with lithium and the electrolyte provides a conducting medium. The membranes are configured in such a way that the cations are separated from the anions in the feed stream. Depending on the application, the concentrate can either be rich in anions or cations. A voltage is applied across the membrane stack, and this determines the movement of cations and anions through the electrodialysis stack. Depending on the layering of cationic and anionic membranes, anions or cations can be extracted from the diluate stream.

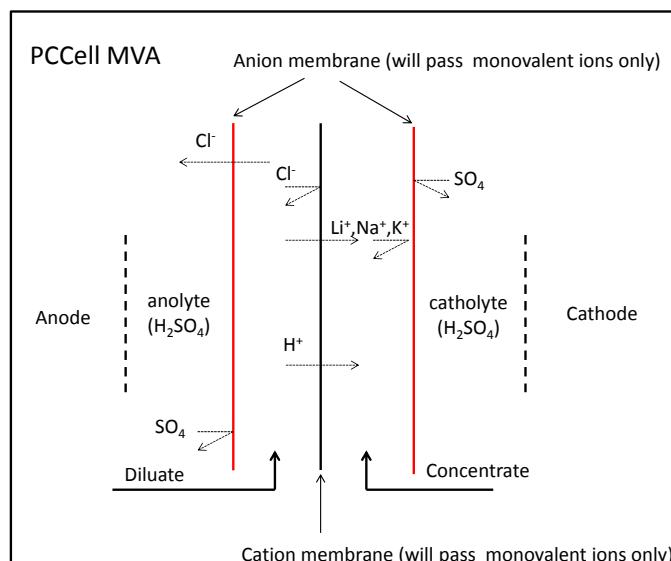


Figure 1: Electrodialysis membrane configuration with movement of ions within the system

2.2 Wairakei Fluid

All fluid used for the experiment was reinjection fluid from the Wairakei Geothermal Field. The fluid was collected at the exit of a heat exchanger which was situated at the Huka Prawn Park (a tourism operator). The fluid temperature varies greatly as the heat demand for the Prawn Park varies throughout the day, with temperature ranges of 60-80°C for the collection of the geothermal brine. A partial chemical analysis of the fluid is shown in Table 1.

Table 1: Typical chemical composition of Wairakei geothermal reinjection fluid.

Element	Al	As	B	Ca	Fe	K	Li	Mg	Na	SiO ₂
Concentration (mg/L)	1.5	6.4	28	18	0.8	165	11	0.1	111	530

2.3 Cell and Membranes

The electrodialysis unit which was used for all of the trials was a two chamber bench top electrodialysis cell unit, PCCell 64002, capable of holding 20 anion and cation membrane pairs (PCCell GmbH). The experimental configuration is shown in Figure 2.

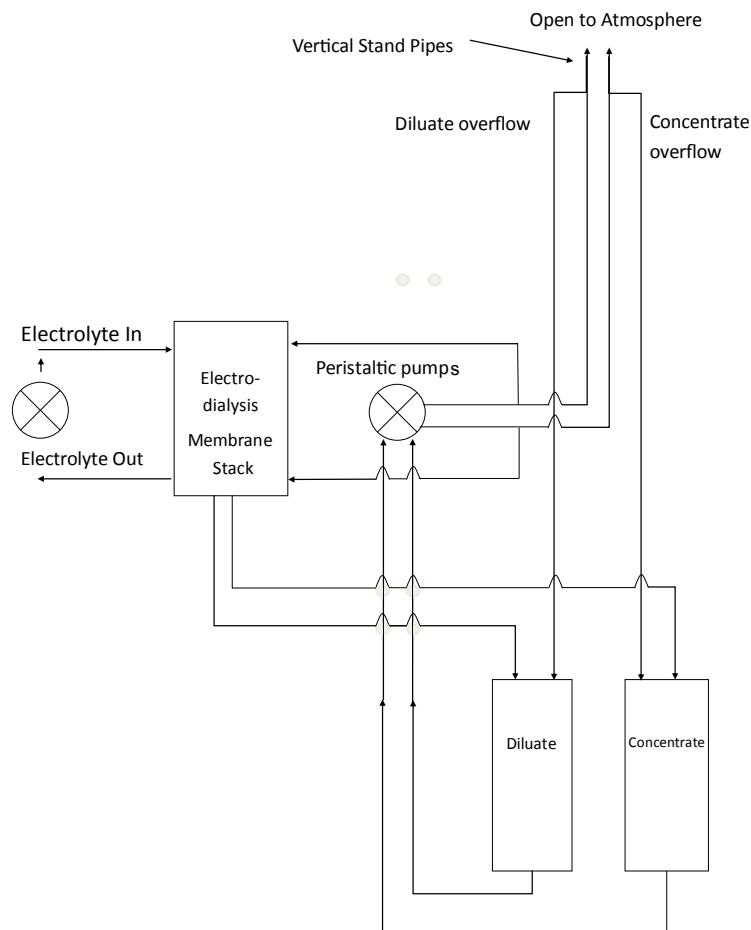


Figure 2: Electrodialysis configuration

The electrodialysis experiments were conducted as a batch process, typically using 2-5 litres per batch. The concentrate, diluate and electrolyte were cycled throughout the system until the diluate was significantly depleted of lithium ions. Usually only one pair of membranes was used but was increased to three pairs at times, when removal efficiency was investigated.

The voltage applied to the electrodialysis unit was supplied by a regulated power supply which allowed for a constant current setting with varying voltage. The power supply maximum was 30 V, above which the current would begin to decrease. For all experiments, the current was fixed with varying voltage.

During the course of the experiments, several different membranes were used, with dimensions of 110x110 mm. DuPont membranes (Nafion) were claimed to be lithium specific and required pre-soaking and cutting before being fitted. However, it was very difficult to cut and orient the membranes correctly within the cell and a complete trial of these lithium specific membranes was not conducted.

The PCCell electrodialysis system was supplied with membranes which required no cutting, as they were specific for the unit. For each membrane pair that was added to the system, an effective membrane surface area of 64 cm² was available for ionic separation. The anode was titanium coated with platinum and the cathode stainless steel to prevent corrosion of the electrodes. The fluids were transported to and from the unit using polypropylene tubing.

2.4 Silica Removal

The colloidal and dissolved silica can cause significant blocking within electrodialysis cells and can damage the membranes. This necessitated removal of silica prior to extraction of lithium. Any silica removal technology could have been used, but the silica was removed by electrocoagulation using aluminium electrodes in the work reported here. Electrocoagulation is an efficient and cheap process to remove silica from the brine (Mroczek et al, 2006). The electrocoagulation time was minimized to avoid lithium co-precipitation.

2.5 Calcium Removal

The production of calcium sulphate can be severely detrimental to the performance of the membranes, as precipitation blocks active ion exchange sites. This interference can be easily removed by addition of either sodium polymetaphosphate or sodium oxalate. The chemical was typically added at the end of the electrocoagulation process where the suspended silica floc would efficiently sweep down the insoluble calcium salts. Both chemicals were effective and caused no decrease in lithium concentration.

Fluid with 385 mg/L of calcium (the highest recorded calcium concentration that was measured within geothermal fluid) was recirculated through the electrodialysis system without calcium removal. This value is relatively low when compared to electrodialysis in whey treatment but large compared to electrodialysis acid recovery systems (e.g. Daufin et al., 2001; Martí-Calatayuda et al., 2014). At this high concentration no crystals were microscopically seen depositing on the surface of the membranes. It was concluded that the concentrations at which the experiments were operated were acceptable, and the removal of the calcium was later discontinued. However, at higher concentrations, calcium removal may still be necessary.

2.6 Chlorine Production

The main detrimental reaction is the formation of chlorine in the anode compartment by oxidation of chloride ion, which can result in destruction of membranes near the anode. At high current densities the overvoltage for oxygen evolution may raise the electrode potential into the region of chlorine production. At times chlorine was evident and accompanied by a strong smell which occurred when the electrodialysis unit was operating. This effect was more pronounced at higher voltages, so the voltage of the system was kept at a minimum to produce less chlorine gas and increase the efficiency of the process.

2.7 pH Control

One of the problems that hindered the success of the experiments and was detrimental to the membranes was high voltage. The power supply controlled the current by varying the voltage and the voltage could increase significantly during a trial.

Figure 1 shows that the flow of diluate at the anode side of a cation membrane allows the transport of protons, as they are small enough to pass through the anion membrane. As a consequence, this progressively decreases the pH of the concentrate. Overall an exchange in the pH between the diluate and concentrate is observed, which is proportional to the volume of each respective stream. The pH increase is caused by reduction of the hydrogen ions at the cathode. Hence the pH of the electrolyte increases and the fluid becomes less conductive; as a consequence voltage increases further.

To counteract the increase in voltage across the system, the conductivity of the fluids must be high. This was achieved by acid dosing with 1 M H₂SO₄. A target between pH 2 and 4 was chosen because this produced sufficient conductivity. However, too low a pH appeared to reduce the mobility of lithium.

The pH of all three fluids within the system changed as the trial progressed. Generally the pH of the diluate and electrolyte increased and the pH of the concentrate decreased to become strongly acidic.

3. EXPERIMENTAL RESULTS

The experiments were conducted at laboratory scale (<10 L) to discover the experimental limitations and ideal experimental conditions. Minimizing the number of variables reduced variations during the experiments and assisted in producing more meaningful and reliable data. All experiments utilizing 1 membrane pair were conducted at constant diluate and concentrate flow rates of 100 mL/min.

3.1 Extraction Efficiency

A typical diluate-concentrate lithium concentration plot is shown in Figure 3 using a large volume of diluate (~10L) and a small volume of concentrate (~1L). The lithium concentration within the diluate decreased to 1.6 ppm which corresponded to an increase in the lithium concentration of the concentrate to 130 ppm.

This showed that the lithium can be almost completely extracted, although complete extraction is not recommended due to decreasing efficiency of extraction. The final concentrations of the streams also surpassed the x20 concentration ratio limit between the concentrate and diluate (PCCell membrane manual). For this solution, the theoretical maximum concentration ratio of diluate to concentrate was about 4.8 to 96 ppm.

Figure 3 also shows that the rate of extraction is fastest when the system has the highest concentration differential. This is seen by the exponential trend with time with the concentrate and diluate reaching equilibrium. Because of this the use of higher concentration diluate fluids was required to ensure that the extraction rate was fast, when initial concentrate concentrations were high.

3.2 Heating

Another aspect which was investigated to increase the extraction efficiency was the preheating of the diluate. This was heated using an electrical coil to 30-40°C. The evidence for a change in the lithium extraction rate at this temperature was inconclusive, although the voltage dropped with increasing temperature. Preheating the fluid decreased the power for the electrodialysis extraction. Although heating of the diluate may appear to be a simple means of increasing process efficiency, care must be taken to prevent any membrane degradation. An upper limit of 60°C is typically given by membrane manufacturers before degradation becomes significant and the life of the membranes is decreased.

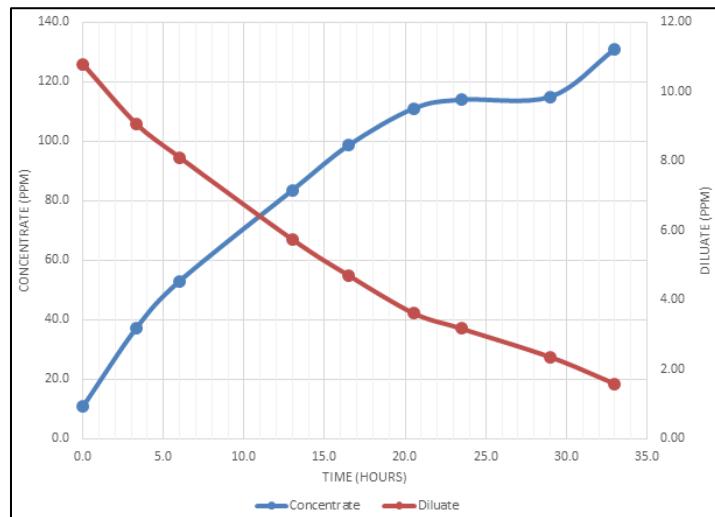


Figure 3: Concentrate and diluate lithium concentrations for an electrodialysis system with one membrane pair and varying voltage.

3.3 Electrodialysis Voltage

The most important characteristic of the electrodialysis cell is the dependence of voltage and current throughout the unit to maximize efficiency. Although larger voltages increase the extraction of the lithium significantly from the brine, a trade-off is encountered with membrane lifetime. Trials were conducted to determine the effective single-pass extraction rate for a given range of currents where the voltage did not exceed 25 V (Figure 4).

This experiment showed that the single pass extraction rate increased significantly with increasing current. Although the extraction values are large for the system at high current, the voltage also needs to be considered. At a current of 0.1 A, the system was still above the recommended 2 V threshold for a single membrane pair configuration. But at this low current setting, the extraction was reduced to less than 0.1 ppm/pass. Strong extraction rates were found at high current and voltage. For example, at a current of 3.7 A and 25 V, a single pass extraction of 2.9 ppm was obtained (at 100 mL/min flow).

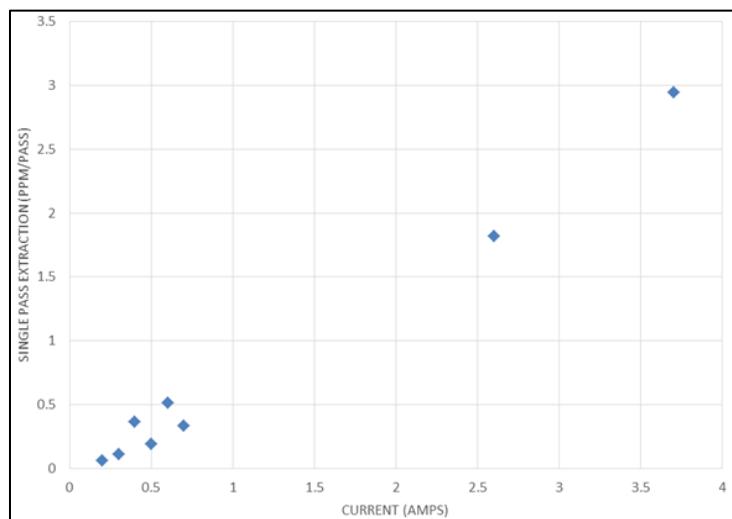


Figure 4: Effect of current/voltage for the single pass extraction of lithium from the electrodialysis unit.

3.6 Membrane Degradation

A major problem which was encountered in the operation of the unit was determining the quality of the membranes. The lifetime of the membrane pairs was expected to be years; however, all membranes used had a significantly lower lifetime (usually less than a month). It is uncertain what the main cause of the decrease in lifetime of the membranes was, but the high voltage trials are suspected to be a leading cause. High voltages also decrease the process efficiency due to electrolysis and chlorine production, which further damage the membranes.

It is also important not to allow the membranes to dry out when not in use. This led to tears within the membranes and caused the flux of lithium and fluid into the electrolyte stream in some experiments.

3.7 Multiple Membrane Stack Electrodialysis Unit

The simplest way to increase the absolute extraction rate was to increase the number of membranes. The unit was filled with 3 membrane pairs each identical supplied by PCCell, (Cation membrane PC MVA-ED 64004-0G00). During these trials the flow rate of the system increased three fold, to 320 mL/min. To increase the efficiency even further, partially evaporated geothermal fluid was used as the diluate for the trials. The evaporation increased the concentrations of dissolved solids and produced a fluid which was highly conductive. This would reduce the operating costs of the process.

The results (Figure 5) show that the efficiency of the process increased with a three membrane pair stack. A total extraction of 180 mg/L of lithium was achieved in less than eight hours with an overall concentrate to dilute ratio of greater than x50. The rate of 0.28 mg/hour.cm² was higher than any previous extraction. The decrease in diluate translated to an increase in concentration of the lithium in the concentrate to 120 ppm, (volumes of diluate and concentrate, 2.5 L and 1.5 L respectively). The discrepancies which arise in the mass balance of lithium ions are due to lithium movement into the electrolyte due to microscopic tears within the membranes. This transferred lithium into the electrolyte stream rather than the concentrate stream.

In previous experiments the extraction of lithium was observed to be highest during the initial stages, when the concentration differential was the lowest. This experiment shows the opposite behaviour. This is believed to have been caused by increasing voltages (>15V) across the electrodialysis membrane stack after the four hours.

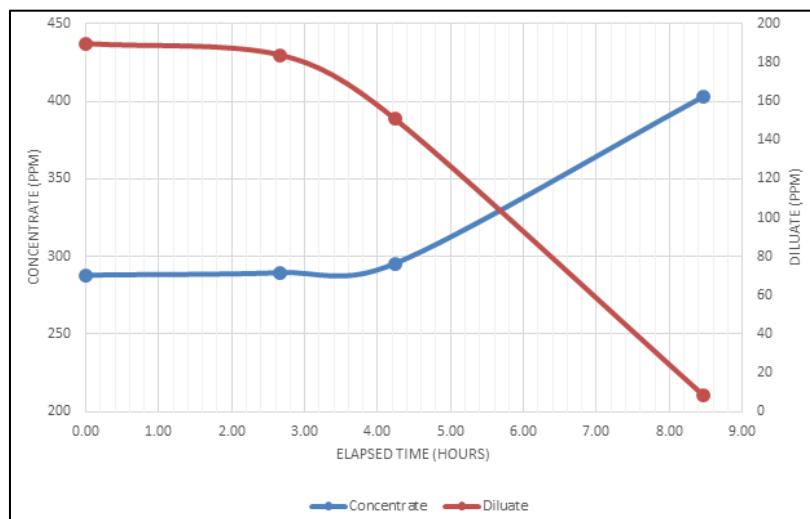


Figure 5: Lithium extraction for a three membrane pair configuration (transfer from diluate to electrolyte evident).

3.8 Summary

A large number of experiments were conducted with the electrodialysis unit, resulting in the following conclusions.

- The acidification of the diluate and concentrate was found to be very beneficial for the extraction of lithium; however, excess acidification reduced extraction efficiency. A pH range of 2-4 was determined to be the most effective.
- Diluate heating did not appear to increase in extraction efficiency. An increase was expected from work reported in literature.
- Large increases in extraction occurred with increased current, but this seemed to drastically degrade the lifetime of the membranes.
- The potential of multi-stack systems was also investigated with higher extraction rates and high lithium concentrations. Of all the trials conducted, the highest lithium flux obtained was 0.28 mg/hour.cm².

4. FURTHER AREAS OF INVESTIGATION

A number of questions remain unanswered in characterizing the electrodialysis of geothermal brines. The effect of heating should be reevaluated as a free source of geothermal heat may increase the efficiency at little additional cost. It has been assumed that the flow rate of the system is believed to only have a small influence, needing only to be turbulent to ensure high diffusion rates. However the effect of flow rate was not investigated and was essentially constant for the duration of the trials. The most difficult

characteristic was determining the ideal voltage and current values for the system. The membranes appeared to quickly suffer irreversible damage, which was probably caused by large current/voltage densities.

Given that the Nafion (Du Pont) lithium specific membranes are commercially available, if these are shown to be effective and reliable then this would avoid the concentrating of other unwanted cations. For most experiments the PCCell membrane used, which were not lithium specific.

5. CONCLUSIONS

Considering the trial results which produced the highest extraction rates, a lithium flux of 0.28 mg/hour.cm² shows that scaling up to a relatively small 1 m² transfer surface area, assuming that the concentration flux is constant throughout the membrane, is equivalent to extracting all of the lithium out of 250 kg of Wairakei brine per hour.

The laboratory experiments showed that after the removal of silica it was possible to extract all of the lithium out of the brine. However, the potential of the overall system as an industrial process cannot be gauged with the small scale laboratory data. To test and understand if concentrating lithium from Wairakei fluid is economically viable, larger scale field pilot plant trials would have to be undertaken.

The potential of heating and evaporation of a primary concentrating unit will also need to be further investigated, which may improve the extraction of lithium.

Electrodialysis is a mature technology that is used extensively in the dairy, food, and potable water industries for the desalination of aqueous streams and the production of edible salt from seawater in Japan. For scaling up to a field pilot plant, expertise from these industries will be sought out to assist optimization of the process so the correct operating procedures are used to provide both sufficient extraction and membrane longevity.

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