INDONESIAN MINING JOURNAL Vol. 26, No. 1, April 2023 : 29 - 37

LITHIUM EXTRACTION FROM DIENG GEOTHERMAL BRINE USING SOLVENT EXTRACTION – A PRELIMINARY STUDY

STUDI PENDAHULUAN: EKSTRAKSI LITIUM DARI FLUIDA PANAS BUMI DIENG MELALUI EKSTRAKSI PELARUT

AGUS WAHYUDI, ANDINA SEPTIARANI, HAIRUNNISA and ISYATUN RODLIYAH
Testing Center for Mineral and Coal, Ministry of Energy and Mineral Resources
Jalan Jenderal Sudirman No. 623 Bandung 40211
Corresponding author's e-mail: a.wahyudi80@gmail.com

ABSTRACT

This preliminary study aims to obtain the lithium compounds from a geothermal brine through a solvent extraction. The brine samples were collected from PT Geodipa Energi Geothermal Power Plant in Dieng, Central Java, Indonesia. The ICP analysis was conducted to measure brine chemical composition. Brine's lithium content was 62.73 ppm with the dominant impurities silica (Si), calcium (Ca), potassium (K), sodium (Na), and boron (B). Silica removal was conducted by centrifugation technic with the addition of flocculants, while calcium removal was achieved by adding sodium carbonate. The CYANEX® 936P was used for the extraction process and was diluted in kerosene (1:1 O/A ratio). The extraction pH was adjusted by adding 10% H_2SO_4 solution (acid condition) and 10% NH_4OH (alkaline condition). The optimum condition for lithium extraction was observed at pH = 11, with the highest lithium recovery of 90%. The eluate from the stripping process was then precipitated by adding Na_2CO_3 to produce lithium carbonate powder.

Keywords: geothermal brines, lithium, solvent extraction.

ABSTRAK

Melalui ekstraksi pelarut, studi pendahuluan ini bertujuan untuk memperoleh senyawa litium dari fluida/brine panas bumi. Percontoh brine diambil dari Pembangkit Listrik Tenaga Panas Bumi PT Geo Dipa Energi di Dieng, Jawa Tengah, Indonesia. Analisis ICP dilakukan untuk mengukur komposisi kimia brine. Kandungan litium brine adalah 62,73 ppm dengan pengotor dominan berupa silika (Si), kalsium (Ca), kalium (K), natrium (Na), dan boron (B). Penghilangan silika dilakukan dengan proses sentrifugasi dan penambahan flokulan, sedangkan proses penghilangan kalsium dilakukan dengan penambahan natrium karbonat. CYANEX® 936P digunakan untuk proses ekstraksi dan dilarutkan dalam kerosin (rasio O/A 1:1). Pengaturan pH saat proses ekstraksi dilakukan dengan menambahkan larutan H_2SO_4 *10% (kondisi asam) dan* NH_4OH *10% (kondisi basa). Kondisi optimum untuk ekstraksi litium terjadi pada pH = 11, dengan perolehan litium tertinggi sebesar 90%. Eluat dari proses stripping kemudian diendapkan dengan menambahkan* Na_2CO_3 *sehingga terbentuk padatan litium karbonat.*

Kata kunci: brine panas bumi, ekstraksi pelarut, litium.

INTRODUCTION

Lithium is the lightest metal element with various versatile applications. One of them is used as component in lithium-ion batteries (LIBs). Therefore, the demand for lithium soars due to the need for LIBs, which power the electric vehicles (EVs). Recently, global lithium consumption reached more than 100,000 tons of lithium carbonate per year and is estimated to be more than 160,000 tons by 2025 (Murodjon *et al.*, 2020; Sujoto *et al.*, 2021). World Bank has predicted the increased demand for energy technologies such as battery minerals will significantly escalate lithium production by more than

Received: 24-03-2023, first revision: 12-04-2023, second revision: 17-04-2023, accepted: 05-05-2023.
DOI: 10.30556/imj.Vol26.No1.2023.1477

450% in 2050 based on 2018 production (Hund *et al.*, 2020).

Lithium can be found in three deposit types: continental brines, sedimentary deposits, and pegmatites (Stringfellow and Dobson, 2021). The global lithium reserves and resource bases are estimated to be 21 million metric tons and 86 million metric tons of lithium, respectively (US Geological Survey, 2020). As most of the lithium is also conserved in brine, geothermal brine is one of the lithium resources with considerable potential (Ji *et al.*, 2017).

Geothermal brine is saltwater within the earth and contains various minerals because it flows between hot fluids and rocks (Bundschuh and Tomaszewska, 2018; Sujoto *et al.*, 2021). Brine from the geothermal power production is sometimes considered a nuisance to the environment because of its highly corrosive minerals and high temperature (Reitenbach, 2015). However, according to the Geological Agency of Indonesia, the Geo Dipa Energi (GDE) Geothermal Power Plant (PLTP) in Dieng Plateau was estimated to have potential as a source of lithium content with a grade value of 50–99 ppm with estimated total lithium production of 360 ton/year (Badan Geologi, 2020).

Lithium extraction from geothermal brines has captured substantial attention because it taps into waste brine after being used for power generation and makes use of existing geothermal facilities to lower production costs. In the US, the Salton Sea area in California is one of the most mineral-rich geothermal brine sources, with the most geothermal plants in the region (Toba *et al.*, 2021).

The methods to extract lithium from brines are mainly precipitation, organic sorbents, organic ion-exchange resins, ion-imprinted polymers, inorganic molecular sieve ion-exchange adsorbents, solvent extraction, membrane, and electrochemical separation (Stringfellow and Dobson, 2021). Among these methods, solvent extraction was considered a promising one to extract the lithium from high magnesium contained brine because of its high selectivity, short equilibration time, low chemical, and energy consumption (Bai *et al.*, 2021). This study aims to obtain lithium compound from Dieng geothermal brine through a solvent extraction.

METHOD

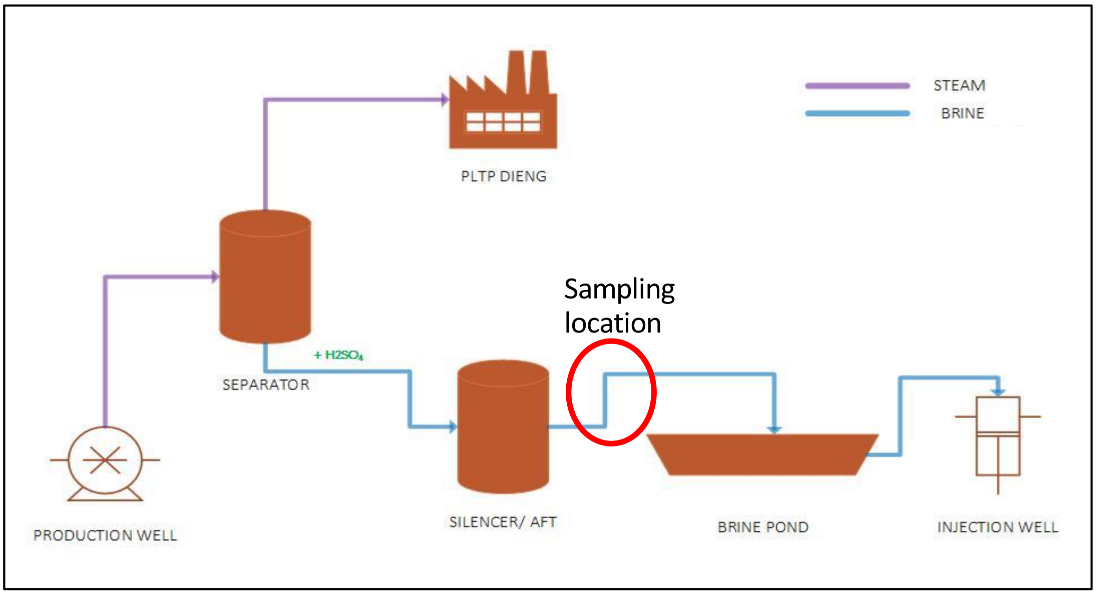
The geothermal brine samples were collected from PT Geo Dipa Energi geothermal power plant, Dieng, Central Java, Indonesia, using a grab method in a brine channel which connects the atmospheric flush tank (AFT) and brine pond (Figure 1).

ICP analysis was conducted to measure the chemical composition of the brine samples. Methods used in processing the brine sample is presented in Figure 2. The first step is silica and calcium removal. The desilication process was conducted using a centrifuge for 20 minutes with flocculant addition around 60 mg/kg, while the calcium removal was achieved by adding sodium carbonate, Na_2CO_3, in the form of powder, up to pH = 10. The treated brine was then carried out the extraction process.

The extraction used a solvent namely CYANEX® 936P obtained from Solvay company and kerosene as the diluent, with a ratio of 40% v/v. It was started by mixing the treated brine with Cyanex-kerosene using 1:1 O/A ratio, creating two immiscible layers. The process was carried out in a beaker glass under varying pH (acidic, default, basic) to find the optimum pH; pH = 3, pH = 5 (default pH of the treated brine), pH = 8,57, and pH = 11, each at the same temperature (55 °C), mixed for 30 minutes. Acidic pH was reached with the addition of 10% H_2SO_4 solution, while 10% NH_4OH was used to increase the pH up to 11. Once the solvent extraction was accomplished, the resulting layers were then transferred into a separating funnel to collect the aqueous phase. One with the higher density at the bottom of the immiscible layers is used to proceed for ICP analysis. The ICP analysis showed whether the lithium concentration in the aqueous phase was reduced, or in other words, successfully transferred into the organic phase at the top of the immiscible layers. The optimum pH condition for the process was indicated from the collected sample (aqueous phase) containing the lowest lithium concentration (at certain pH).

Having done the varying pH extraction and obtained the optimum pH condition, the resulting organic phase at the optimum pH was then stripped using diluted H_2SO_4 (1 M) at 55 °C, mixed for 30 minutes in a beaker glass to release the extracted lithium back into the aqueous phase. Once the stripping was completed, two immiscible layers formed and then transferred into the separating funnel. The lower layer (aqueous phase) was then collected to observe the lithium concentration using ICP analysis.

The eluate collected from the stripping process was then added with solid Na_2CO_3 in a beaker glass at 80–90 °C and pH = 12–14 until a white powdery precipitate was formed (Li-carbonate). This process was then followed by filtration to separate the white precipitate from the filtrate. The precipitated white powder was then proceeded to XRD analysis to observe the formation of Li-carbonate.



Source: Badan Geologi (2020) (modified)

Figure 1. Sampling location for geothermal brine

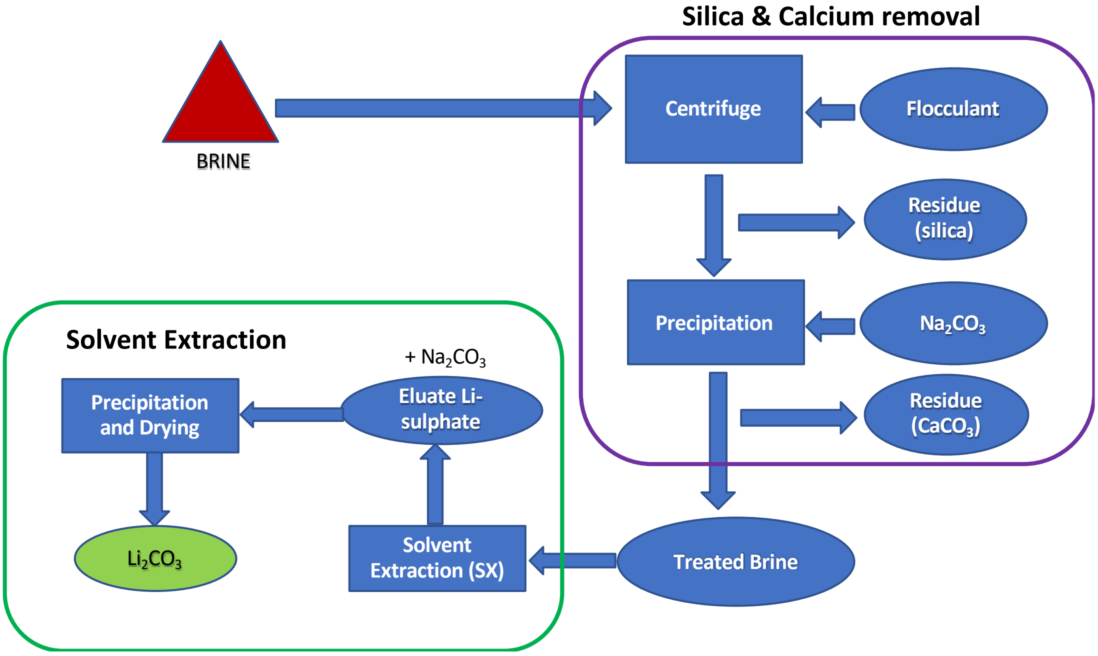


Figure 2. The method used in lithium extraction from geothermal brine

RESULTS AND DISCUSSION

Table 1 shows the chemical composition of Dieng geothermal brine. The lithium content of the brine sample is 62.73 ppm and the dominant impurities are silica (Si), calcium (Ca), potassium (K), sodium (Na), and boron (B).

Prior to lithium extraction using solvent extraction, the brine was added by flocculant to remove the silica colloids (Figure 3). This is important because the colloids inhibited the selective recovery of lithium from the geothermal water. Thus, controlling the concentrations of SiO_2 ions in geothermal reservoirs is suggested for the efficient operation of geothermal systems and the successful recovery of lithium from the geothermal brine (Lee and Chung, 2022).

The initial silica concentration in the brine geothermal water used in this study was 630 ppm. With the addition of a flocculant followed by 5 – 30 minutes centrifugation, the concentration of silica decreased by 86% to as low as 90 ppm. Added flocculant allowed silica colloids to form larger agglomerated material than the fluids so that it was easier to be separated by gravity. Centrifugation done in this study helped the mechanical separation in a short time. After the desilication, the geothermal brine became clearer with no colloidal substances that can be observed visually.

Besides silica, calcium was also precipitated from the brine by adding sodium carbonate up to pH = 10 (Figure 4a). White solid calcium carbonate was then formed in the bottom of the beaker glass (Figure 4b). The process was able to decrease the calcium content of the brine sample from 650 ppm to 7.51 ppm.

The treated brine was then carried out the extraction process. Several methods to extract the lithium from the brine have been investigated, including precipitation, adsorption, solvent, ionic liquid, membrane, electrochemical, and chromatographic techniques (Warren, 2021). However, solvent extraction was proposed for the extraction of lithium from aqueous solutions of alkali metal salts as early as 1954, due to its selectivity, short equilibration time, and low chemical, and energy consumption (Bai *et al.*, 2021; Stringfellow and Dobson, 2021).

Table 1. Chemical composition of Dieng geothermal brine sample (ppm)

Si	Fe	Ca	Mg	K	Na	Mn	Li	B	As	S
630	3.92	650	0.97	2,800	9,420	14.98	62.73	550	80.07	43

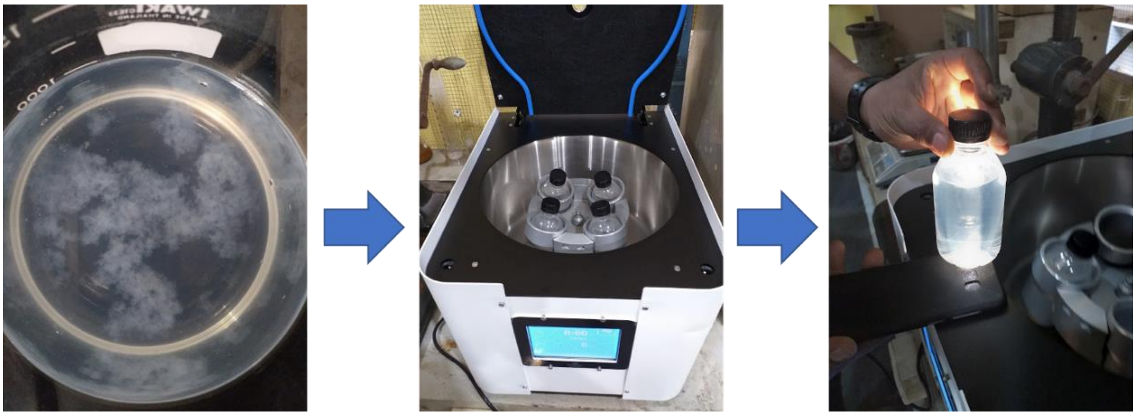


Figure 3. Desilication process of the brine geothermal water: (a) flocculant addition; (b) centrifugation; (c) post-desilication

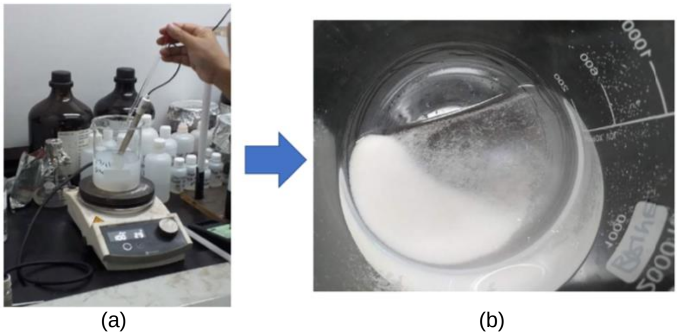

(a) (b)

Figure 4. Calcium precipitation process by adding the sodium carbonate (a); formed white solid calcium carbonate (b)

The solvent extraction method uses the transfer of a compound from one liquid phase to another based on the compound's different solubility or distribution coefficients (Meng *et al.*, 2021). The solvent extraction or liquid-liquid extraction method was used due to the simplicity of the process and the relatively short operation time (Masmoudi *et al.*, 2020). In this study, the contact time was only 30 minutes, supported by many studies showing that a contact time of less than an hour was adequate for the process. In addition, the recyclability of the solvent makes this method beneficial. Thus, many industries have extensively used this method to recover valuable metal ions from solutions because it is promising, requires low energy consumption, and is easy to apply. Researchers have used various solvents to extract specific metal ions from aqueous solutions (Zhou *et al.*, 2019; Lee and Chung, 2022).

Optimum lithium recovery parameters will vary based on the target geothermal fluids' specific physical and chemical properties (Warren, 2021). If some ionic species are not soluble in the extract, higher extraction efficiency can be achieved by changing the pH of the raffinate. By changing the pH of the extraction system, the distribution coefficient of the solute can be altered to favor partitioning into the extract (Rupasinghe, 2016). In other words, the distribution ratio can be changed by changing the acidity or pH (Maimulyanti and Prihadi, 2014). The extraction efficiency is indicated by the fraction of extracted substances, i.e., percent extraction. Therefore, a different pH was used in this study to obtain the optimum extraction condition.

From the varying pH extraction, there was a difference in the colors of the brine sample and solvent before (Figure 5) and after the extraction (Figure 6).

Figure 5. Two immiscible layers before the extraction

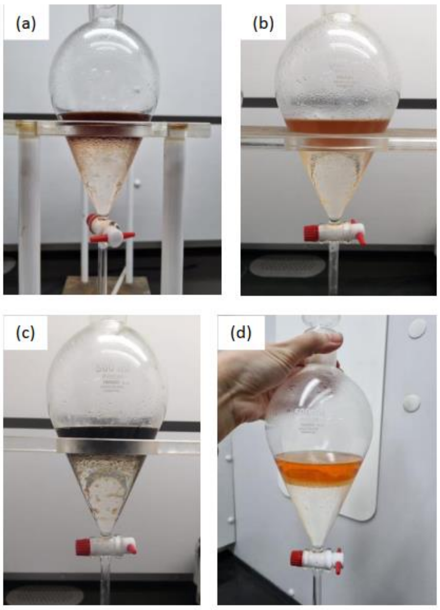


Figure 6. Two immiscible layers after the extraction, at: (a) pH = 3 ; (b) pH = 5 ; (c) pH = 8,75; (d) pH = 11

Lithium exists as a cationic species, Li^+, which is difficult to selectively extract due to its strong tendency to be hydrated. Various acidic and neutral commercial extractants have been used to extract the Li(I) from brines, sea waters, and alkaline solutions (Nguyen and Lee, 2018). During the solvent extraction, lithium ions on the brine exchange with the extractant contained in the organic liquid phase and form complexes (Warren, 2021). Several researchers have reported the extraction of Li(I) using a mixture of chelating and neutral extractants such as tributyl phosphate (TBP) and trioctylphosphine oxide (TOPO) in kerosene (Nguyen and Lee, 2018). In this study, CYANEX® 936P was used because it was a phosphorus-based extractant specifically formulated for lithium (Li). It forms a complex with Li at any Li selectively concentration as follows:

$$Li^+{}_{(aq)} + RH_{(org)} \leftrightarrow RLi_{(org)} + H^+{}_{(aq)}$$

CYANEX® 936P works on any lithium stream exempt of divalent ions. Kerosene was used as the solvent and the extraction carried out at different pH(s) resulting different recoveries of lithium as illustrated in Figure 7.

Based on Figure 7, the optimum condition for lithium extraction was observed at pH = 11 with the highest lithium recovery of 90%. Similar result was also observed by Harvianto (2014), more than 70% of lithium ion could be extracted at pH 10.6 from seawater using TTA–TOPO in kerosene as the extractant. The efficiencies increase with increasing pH of the aqueous solutions and reach higher than 90% when pH is above 10.2, while the reverse was true with decreasing pH. This phenomenon could be explained by the bonding mechanism of extractants with other dominant metallic ions (K^+, Na^+, Ca^{2+}, Mg^{2+}). The dominant metallic ions generally reduce the extraction efficiency of lithium ion and has a greater effect in the lower pH range. This was also supported by Lee and Chung research report in 2022, that various divalent cations and silicate ions that exist in geothermal water can have an adverse effect on the efficiency of lithium extraction.

Afterward, the stripping process was carried out at pH = 11, resulting in the eluate of lithium-rich solution with 98% recovery. Similar to the extraction, the stripping process also resulted in two immiscible layers. It is an important step to unload the solute, i.e. lithium ions, from the solvent and to recover the solvent for recycling. According to Harvianto (2014), the extraction and stripping steps depend on the kinetics of mass transfer. After the lithium ions were released back into the aqueous phase, the two immiscible layers (Figure 8) were then transferred into the separating funnels to make the collection phase easier (Figure 9).

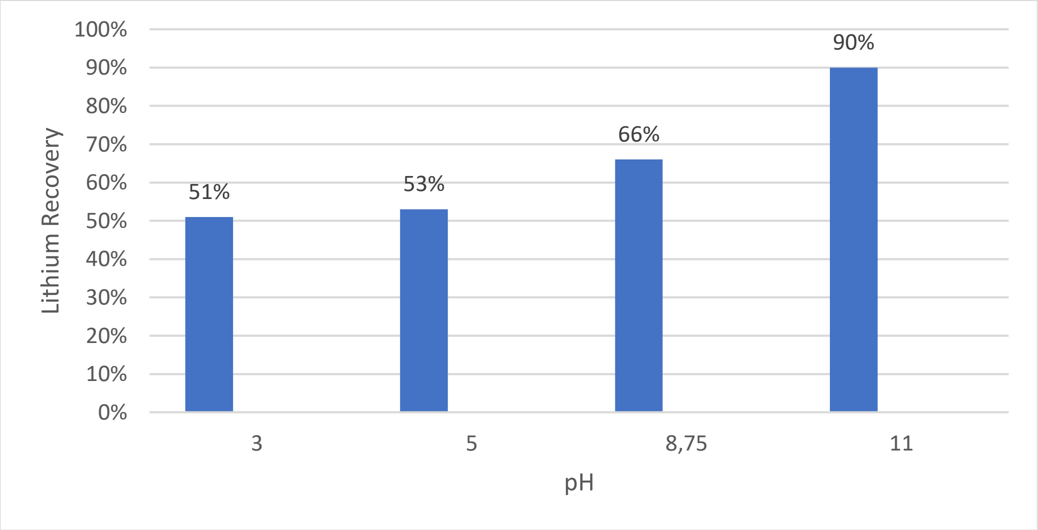


Figure 7. Recovery of lithium as a pH function

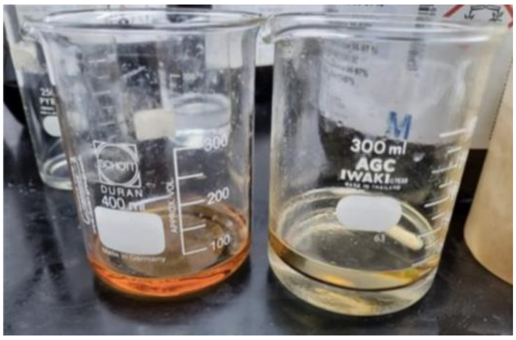


Figure 8. The organic phase from the extraction process: prior to (left measuring cuo) and after (right measuring cup) stripping

Figure 9. Two immiscible layers of organic and inorganic phases as a result of the stripping process

The eluate collected from the stripping process was then added with sodium carbonate in a beaker glass at 80–90 °C and pH = 12–14 until a white powdery precipitate was formed (Figure 10). This process was then followed by filtration to separate the white precipitate (Li-carbonate) from the filtrate. However, it was observed by the XRD analysis that the solid phase produced from the final process still contains impurities in the form of carbonate (gregoryite) and calcium carbonate (calcite) (Figure 11). The presence of sodium carbonate might be caused by the excess addition of precipitating reagents during calcium removal, while the calcium carbonate might be incorporated along the filtration. Harvianto (2014) stated that the extraction efficiencies of lithium ion decrease with dominant ions in an order of Cl^-, K^+, Na^+, Ca^{2+} and Mg^{2+}.

Figure 10. Precipitation process of lithium carbonate with the addition of sodium carbonate

Figure 11. Lithium carbonate powder produced from the precipitation process

The character of the solvent extraction system used was only selective for lithium against other monovalent cations, but higher-valent cations are extracted ahead of lithium. Therefore, higher valent cations (Ca^{2+}, Mg^{2+}, etc.) need to be fully removed from the brine ahead of the solvent extraction step. One may consider using membrane technology, the selection must be based on the membrane's ability to allow monovalent cations to pass while blocking the passage of higher-valent ions.

CONCLUSION AND SUGGESTION

The lithium content of Dieng geothermal brine was 62.73 ppm with the dominant impurities silica (Si), calcium (Ca), potassium (K), sodium (Na), and boron (B). The optimum condition for lithium extraction was observed at pH = 11, with the highest lithium recovery of 90%. The stripping process succeeded with 98% recovery with two immiscible layers. The precipitation of lithium from the eluate was conducted by adding sodium carbonate and resulted in lithium carbonate powder. The solvent extraction system used was selective for lithium against other monovalent cations. However, higher-valent cations were still extracted, so they must be entirely removed from the brine before the solvent extraction step.

ACKNOWLEDGEMENT

The authors wish to thank the Ministry of Energy and Mineral Resources, Republic of Indonesia for funding the research. The authors also thank PT Geo Dipa Energy for the brine geothermal samples and Solvay for the free sample Cyanex 936P for the lithium extraction process.

REFERENCES

Badan Geologi (2020) ‘Potensi litium di Indonesia’, in *Webinar Potensi Pemanfaatan Litium untuk Baterai Ion-Li di Indonesia*. Bandung: Badan Geologi.

Bai, R., Wang, J., Wang, D., Zhang, Y. and Cui, J. (2021) ‘Selective separation of lithium from the high magnesium brine by the extraction system containing phosphate-based ionic liquids’, *Separation and Purification Technology*, 274, p. 119051. Available at: https://doi.org/10.1016/j.seppur.2021.119051.

Bundschuh, J. and Tomaszewska, B. (eds) (2018) *Geothermal water management*. London: CRC Press.

Harvianto, G.R. (2014) *A comprehensive study on solvent extraction of lithium ion from aqueous solution and its application in seawater*. Pukyong National University.

Hund, K., Porta, D. La, Fabregas, T.P., Laing, T. and Drexhage, J. (2020) *Minerals for climate action: The mineral intensity of the clean energy transition*. Washington DC: World Bank.

Ji, Z.-Y., Yang, F.-J., Zhao, Y.-Y., Liu, J., Wang, N. and Yuan, J.-S. (2017) ‘Preparation of titanium-base lithium ionic sieve with sodium persulfate as eluent and its performance’, *Chemical Engineering Journal*, 328, pp. 768–775. Available at: https://doi.org/10.1016/j.cej.2017.07.047.

Lee, J. and Chung, E. (2022) ‘The effect of silicate ions on the separation of lithium from geothermal fluid’, *Frontiers in Chemical Engineering*, 4. Available at: https://doi.org/10.3389/fceng.2022.741281.

Maimulyanti, A. and Prihadi, A.R. (2014) ‘Effect of pH on extraction efficiency and distribution in nickel ion separation using solvent extraction’, in E. Rijanto (ed.) *Proceeding ASEAN COSAT 2014*. Jakarta: LIPI Press, pp. 515–522.

Masmoudi, A., Zante, G., Trébouet, D., Barillon, R. and Boltoeva, M. (2020) ‘Understanding the mechanism of lithium ion extraction using tributyl phosphate in room temperature ionic liquid’, *Solvent Extraction and Ion Exchange*, 38(7), pp. 777–799. Available at: https://doi.org/10.1080/07366299.2020.1788201.

Meng, F., McNeice, J., Zadeh, S.S. and Ghahreman, A. (2021) ‘Review of lithium production and recovery from minerals, brines, and lithium-ion batteries’, *Mineral Processing and Extractive Metallurgy Review*, 42(2), pp. 123–141. Available at: https://doi.org/10.1080/08827508.2019.1668387.

Murodjon, S., Yu, X., Li, M., Duo, J. and Deng, T. (2020) ‘Lithium recovery from brines including seawater, salt lake brine, underground water and geothermal water’, in P. Vizureanu (ed.) *Thermodynamics and Energy Engineering*. IntechOpen. Available at: https://doi.org/10.5772/intechopen.90371.

Nguyen, T. and Lee, M. (2018) ‘A review on the separation of lithium ion from leach liquors of primary and secondary resources by solvent extraction with commercial extractants’, *Processes*, 6(5), p. 55. Available at: https://doi.org/10.3390/pr6050055.

Reitenbach, G. (2015) *Mining for lithium in geothermal brine: Promising but pricey*, *powermag.com*. Available at:

https://www.powermag.com/mining-for-lithium-in-geothermal-brine-promising-but-pricey/ (Accessed: 14 February 2022).

Rupasinghe, T. (2016) ‘Liquid Extraction: Acidic Extraction’, in M.R. Wenk (ed.) *Encyclopedia of Lipidomics*. Dordrecht: Springer Netherlands, pp. 1–2. Available at: https://doi.org/10.1007/978-94-007-7864-1_93-1.

Stringfellow, W.T. and Dobson, P.F. (2021) ‘Technology for the recovery of lithium from geothermal brines’, *Energies*, 14(20), p. 6805. Available at: https://doi.org/10.3390/en14206805.

Sujoto, V.S.H., Sutijan, Astuti, W., Mufakhir, F.R. and Petrus, H.T.B.M. (2021) ‘Lithium recovery from synthetic geothermal brine using electrodialysis method’, *IOP Conference Series: Earth and Environmental Science*, 882(1), p. 012003. Available at: https://doi.org/10.1088/1755-1315/882/1/012003.

Toba, A.-L., Nguyen, R.T., Cole, C., Neupane, G. and Paranthaman, M.P. (2021) ‘U.S. lithium resources from geothermal and extraction feasibility’, *Resources, Conservation and Recycling*, 169, p. 105514. Available at: https://doi.org/10.1016/j.resconrec.2021.105514.

US Geological Survey (2020) *Mineral commodities summary*. Reston VA.

Warren, I. (2021) *Techno-economic analysis of lithium extraction from geothermal brines*. Golden, CO. Available at: https://www.nrel.gov/docs/fy21osti/799178.pdf.

Zhou, Z., Liu, H., Fan, J., Liu, X., Hu, Yafei, Hu, Yulei, Wang, Y. and Ren, Z. (2019) ‘Selective extraction of lithium ion from aqueous solution with sodium phosphomolybdate as a coextraction agent’, *ACS Sustainable Chemistry & Engineering*, 7(9), pp. 8885–8892. Available at: https://doi.org/10.1021/acssuschemeng.9b00898.