Applied Chemical Engineering (2026) Volume 9 Issue 1 ISSN: 2578-2010 (O)
doi: 10.59429/ace.v9i1.5892

ORIGINAL RESEARCH ARTICLE

Polythermal phase equilibria in the Na_2CO_3-LiCl-H_2O ternary system and crystallization of lithium carbonate

Bakhodir Abdullayev[1,6,*], Dilnoza Axmedova[1], Jurabek Bozorov[1], Sarvar Abdiyev[1], Sanat Samatov[1], Erkin Yakubov[2], Khusniddin Botirov[3], Murodullo Rakhimov[4], Elbek Mavlanov[4], Tolmas Olimov[4], Odil Mamajonov[4], Mansur Axmedov[4], Miyasar Zhumanova[4], Shavkat Umarov[5], Sarvigul Khujanazarova[6], Murodjon Samadiy[6]

[1] *University of Economics and Pedagogy, Karshi, 180119, Uzbekistan*

[2] *Karshi State University, Karshi, 180119, Uzbekistan*

[3] *Asian Technology University, Karshi, 180119, Uzbekistan*

[4] *Tashkent Chemical of Technological Institute, Tashkent, 100001, Uzbekistan*

[5] *Jizzakh State Pedagogical University, Jizzakh, 130100, Uzbekistan*

[6] *Karshi State Technical University, Karshi, 180119, Uzbekistan*

***Corresponding author:** Bakhodir Abdullayev, bahodir.abdullayev.92@mail.ru

ARTICLE INFO

Received: 21 January 2026
Accepted: 11 February 2026
Available online: 28 February 2026

ABSTRACT

Understanding the phase equilibria and solubility behavior in multicomponent salt-water systems is essential for the development of efficient separation and resource recovery technologies, especially for lithium-containing compounds. However, reliable phase equilibrium data for the Na_2CO_3–LiCl–H_2O system remain limited over a wide range of temperatures and concentrations. In this study, solubility relationships and phase transformations in the sodium carbonate–lithium chloride–water system were systematically studied using a visual polythermal method over a wide range of temperatures and compositions. The resulting phase diagram describes distinct crystallization regions corresponding to ice, $Na_2CO_3 \cdot 10H_2O$, $Na_2CO_3 \cdot 7H_2O$, $LiCl \cdot 5H_2O$, $LiCl \cdot 2H_2O$, $LiCl \cdot H_2O$, and the newly identified Li_2CO_3 phase. The formation and stability of the new lithium carbonate phase were confirmed using combined chemical and physicochemical analysis, including infrared spectroscopy and X-ray diffraction, ensuring the reliability of the obtained equilibrium data. Characteristic absorption bands in the IR spectrum observed at 1437.03 cm^{-1} and 869.93 cm^{-1} were assigned to carbonate functional groups, providing further evidence for the formation of Li_2CO_3. The polythermal diagram shows that a significant portion of the system is occupied by crystallization fields, indicating the initially low solubility of lithium carbonate. This behavior highlights the possibility of selectively separating Li_2CO_3 from saturated solutions through controlled evaporation. Overall, the results provide fundamental thermodynamic insights and practical recommendations for lithium recovery processes and the development of effective separation strategies in aqueous carbonate-chloride systems.

Keywords: Lithium chloride; evaporation; sodium carbonate; cooling; precipitation

1. Introduction

In addition to being one of the rarest elements, lithium also has a high price[1]. The main cause of this is the rise in electric vehicle production. The amount of lithium used worldwide to make lithium batteries has already surpassed 46% and is expected to reach over 2 million tons by 2030[2]. Water sources will need to be utilized in the production of lithium as a raw material to meet the global demand for the metal. Lithium reserves make up 70-80% of the world's total reserves, and salt lake brines, geothermal waters, and sea and ocean waters are all excellent raw materials for lithium extraction[3].

Despite having a total lithium content of over 2600 billion tons, sea and ocean water only contains 0.1 to 0.2 parts per million of lithium and is not currently utilized for industrial lithium extraction[4-9]. Geothermal waters have a lithium content of no more than 100 parts per million[10,11].

However, the high concentration of different impurities in them prevents the large-scale use of geothermal waters[12]. The salt lakes have the highest concentration, with up to 1000 parts per million of lithium. Lithium extraction is made more difficult by the presence of alkali and alkaline earth elements, particularly magnesium, in brines[13,14]. Up to 80% of the global market is made up of lithium compounds like hydroxide, carbonate, and chloride, which are highly sought after[15]. Due to the widespread availability and lower cost of lithium isolation, aqueous solutions containing large amounts of lithium are a more popular method of obtaining lithium[16]. Information about how lithium compounds behave in aqueous solutions when they are concentrated is necessary for this.

The system of Na_2CO_3-LiCl-H_2O was examined using the visual polythermal analysis method to physicochemically support the behavior of lithium chloride across a broad range of temperatures and concentrations[17].

2. Materials and methods

The work used sodium carbonate that had been double recrystallized. An X-ray diffractometer (XRD, Lab XRD-6100, Shimadzu Co., Ltd., Japan) was used to identify the sample, revealing that the spectrogram is identical to that of the standard product. Using a chemical method and an analytical check on an inductively coupled plasma optical emission spectrometer (ICPOES, Prodigy, Leman Co., USA), the purity of the doubly recrystallized lithium chloride was ascertained. Using a sparkling water system (ULUP-11-10T, Ulupur Technologies Co. Ltd., China), the water was freshly ionized distilled water (DDW). The TL-15 alcohol glass thermometer was used in the temperature range of -100 to 20 °C, and the study was conducted using the visual-polythermic method.

3. Results and discussion

The eight internal cuts were used to study solubility in the Na_2CO_3–LiCl-H_2O system. Sections 5–8 are drawn from the top of LiCl to the side of Na_2CO_3–H_2O, and Sections 1–4 are drawn from the top of Na_2CO_3 to the side of LiCl–H_2O. -70, -60, -50, -40, -30, -10, 0, 10, 20, and 30 °C solubility isotherms. **Figure 1** displays the polythermal complete diagram of the Na_2CO_3-LiCl-H_2O system, which was constructed at temperatures ranging from -80.2 °C to 38.0 °C based on the binary system data and internal sections.

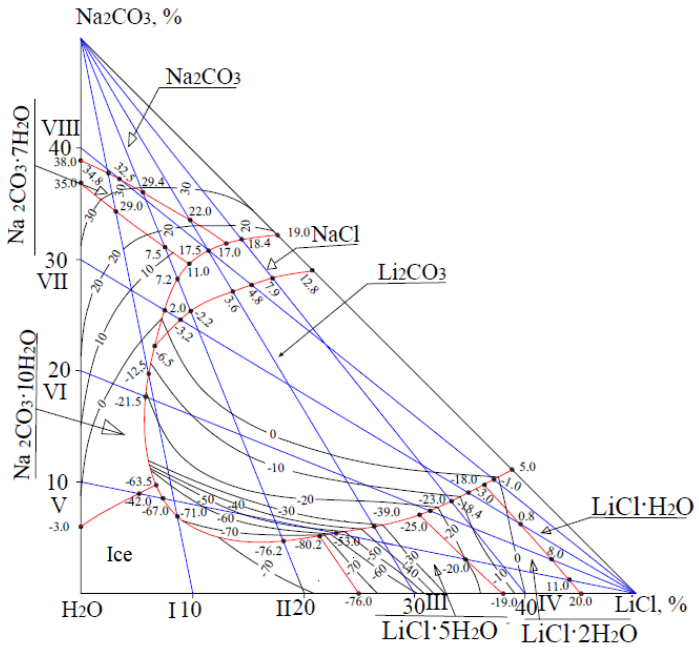

Figure 1. Diagram of the Na_2CO_3-LiCl-H_2O system's solubility.

The field of ice crystallization, $Na_2CO_3 \cdot 10H_2O$, $Na_2CO_3 \cdot 7H_2O$, Na_2CO_3, $LiCl \cdot 5H_2O$, $LiCl \cdot 2H_2O$, $LiCl \cdot H_2O$, and the new phase Li_2CO_3 are delimited based on the observations of the polythermal solubility diagram. Lithium carbonate precipitate forms through a double displacement reaction between sodium carbonate and lithium chloride, expressed as: $Na_2CO_3 + 2LiCl \rightarrow Li_2CO_3 \downarrow + 2NaCl$. The formation of a solid phase is primarily governed by the low solubility of lithium carbonate in water. At 20 °C, its solubility is limited (approximately 1.33 g per 100 mL, decreasing to about 0.72 g per 100 mL under comparable conditions), which promotes rapid supersaturation and subsequent crystallization. Consequently, lithium carbonate readily separates from the solution as a precipitate, enabling its efficient recovery through controlled crystallization processes. **Table 1** displays the equilibrium solution compositions and corresponding crystallization temperature at the six triple nodal points where these fields converge.

Table 1. The Na_2CO_3-LiCl-H_2O system's double and triple points.

The composition of the			Crystallization temperatures, °C	Solid phase
Na_2CO_3	LiCl	H_2O		
7.0	-	93.0	-3.0	Ice+Na_2CO_3
9.5	6.4	84.1	-42.0	Ice+$Na_2CO_3 \cdot 10H_2O$
10.4	7.6	82.0	-63.5	Ice+$Na_2CO_3 \cdot 10H_2O$+Li_2CO_3
18.8	6.8	74.4	-21.5	$Na_2CO_3 \cdot 10H_2O$+Li_2CO_3
20.0	6.0	74.0	-12.8	-
25.2	9.2	65.6	2.0	-
28.2	10.4	61.4	7.2	-
29.4	11.2	59.4	11.0	$Na_2CO_3 \cdot 7H_2O$+$Na_2CO_3 \cdot 10H_2O$+Li_2CO_3
30.2	9.0	60.8	7.5	$Na_2CO_3 \cdot 7H_2O$+$Na_2CO_3 \cdot 10H_2O$
35.5	3.0	61.5	29.0	$Na_2CO_3 \cdot 7H_2O$ +$Na_2CO_3 \cdot 10H_2O$
37.0	-	63.0	35.0	Ice+Na_2CO_3
30.2	12.0	57.8	17.5	$Na_2CO_3 \cdot 7H_2O$+Li_2CO_3
31.2	12.0	56.8	17.0	$Na_2CO_3 \cdot 7H_2O$+$Na_2CO_3 \cdot H_2O$+Li_2CO_3
33.8	11.5	54.7	22.0	$Na_2CO_3 \cdot 7H_2O$+$Na_2CO_3 \cdot H_2O$

The composition of the			Crystallization temperatures, ℃	Solid phase
Na_2CO_3	LiCl	H_2O		
38.4	4.4	57.2	32.5	$Na_2CO_3·7H_2O+Na_2CO_3·H_2O$
38.9	3.5	57.6	34.8	$Na_2CO_3·7H_2O+Na_2CO_3·H_2O$
39.0	-	61.0	38.0	$Ice+Na_2CO_3$
33.1	18.8	48.1	19.0	$Na_2CO_3·H_2O+Li_2CO_3$
9.4	8.5	82.1	-67.0	$Ice+Li_2CO_3$
8.4	9.6	82.0	-71.0	$Ice+Li_2CO_3$
6.2	18.0	75.8	-70.0	$Ice+Li_2CO_3$
6.4	22.1	71.5	-80.2	$Ice+Li_2CO_3+LiCl·5H_2O$
-	25.0	75.0	-76.0	$Ice+LiCl·5H_2O$
6.6	26.2	67.2	-53.0	$Li_2CO_3+LiCl·5H_2O$
-	-	-	-39.0	$Li_2CO_3+LiCl·5H_2O$
7.6	31.4	61.0	-25.0	$Li_2CO_3+LiCl·5H_2O+LiCl·2H_2O$
3.8	36.4	59.8	-20.0	$LiCl·5H_2O+LiCl·2H_2O$
-	38.9	61.1	-19.0	$Ice+LiCl·2H_2O$
10.4	35.6	54.0	-18.0	$Li_2CO_3+LiCl·2H_2O$
10.0	37.4	52.6	-3.0	$Li_2CO_3+LiCl·2H_2O+LiCl·H_2O$
8.1	38.5	53.4	0.8	$LiCl·2H_2O+LiCl·H_2O$
4.6	41.8	53.6	8.0	$LiCl·2H_2O+LiCl·H_2O$
2.6	42.9	54.5	11.0	$LiCl·2H_2O+LiCl·H_2O$
-	43.0	57.0	20.0	$Ice+LiCl·H_2O$
11.2	37.8	51.0	-1.0	$Li_2CO_3+LiCl·H_2O$
12.1	38.8	49.1	5.0	$Li_2CO_3+LiCl·H_2O$

Table 1. (*Continued*)

Next, physicochemical studies of lithium carbonate were carried out. **Figure 2** shows an X-ray diffraction pattern of lithium carbonate.

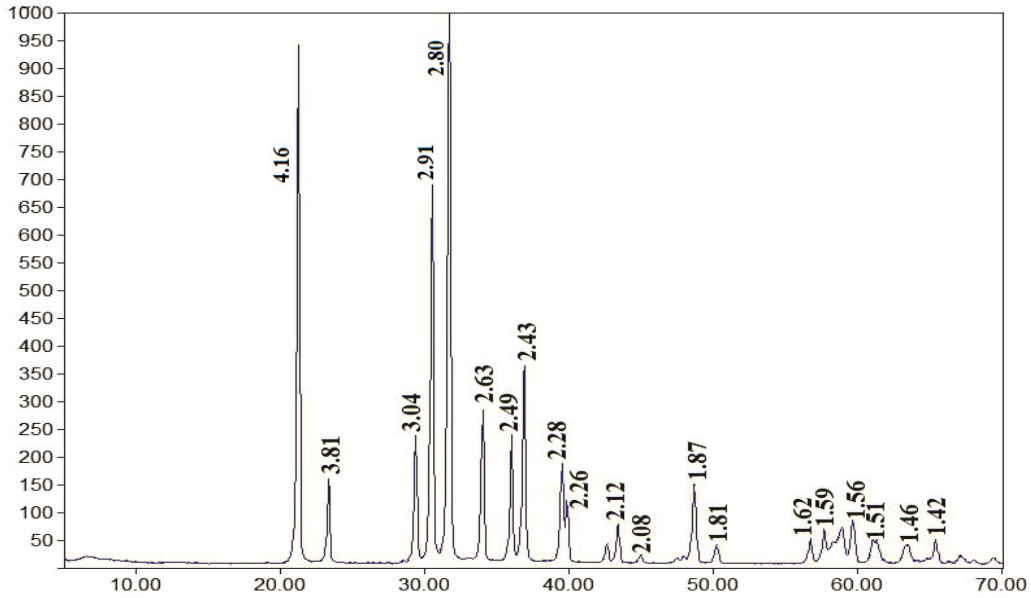

Figure 2. X-ray of lithium carbonate.

The X-ray diffraction (XRD) patterns were interpreted using an X-ray mineral identification database to determine the crystalline phases present. The diffraction profile of lithium carbonate exhibited characteristic reflections with interplanar spacings (d-values) at 4.16, 2.91, and 2.80 Å, which are consistent with the standard pattern of Li_2CO_3 and confirm its formation. To further elucidate the structural features of the synthesized material, infrared (IR) spectroscopy was employed (**Figure 3**). This complementary analysis provided additional evidence of the compound's molecular structure and supported the phase identification obtained from the XRD results.

Figure 3. Lithium carbonate analysis using infrared spectroscopy.

The infrared (IR) spectrum of Li_2CO_3 exhibits characteristic absorption bands at 1437.03 cm^{-1} and 869.93 cm^{-1}, which are attributed to the vibrational modes of carbonate (CO_3^{2-}) groups. The observed broadening of these bands is associated with intermolecular interactions within the crystal lattice, reflecting the structural environment of the mineral phase. Furthermore, the results of the chemical analysis are consistent with the spectroscopic data, thereby confirming the composition and structural integrity of the synthesized lithium carbonate.

Thermal analysis of lithium carbonate was carried out up to 900 °C at a rate of 10 °C per minute. The thermogram of the product is shown in **Figure 4**.

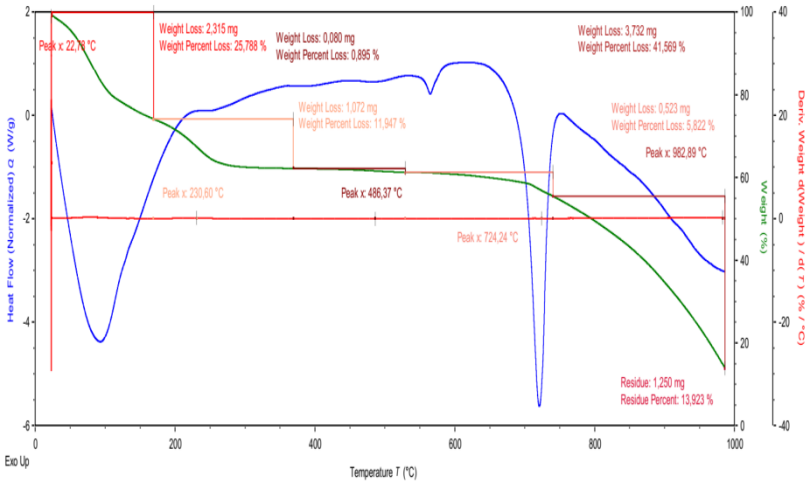

Figure 4. Lithium carbonate analysis using infrared spectroscopy.

When Li_2CO_3 was heated in the presence of air, water, and gas molecules were desorbed. Oxidation occurred with an increase in temperature to 430 °C. Oxidation occurs in the process of thermal explosion. After the temperature interval of Li_2CO_3 heating, its oxidation accelerates. The exoeffect increases with increasing temperature, reaching its peak at 711 °C. After the decomposition of lithium carbonate (680°C), an exothermic effect is observed (maximum 711°C), as shown in the thermogram. According to calculations, the decomposition of lithium carbonate is an endothermic process absorbing 226.3 kJ/mol.

Figure 5 shows a photomicrograph of lithium carbonate, which shows more light spots, which are caused by the formation of lithium carbonate.

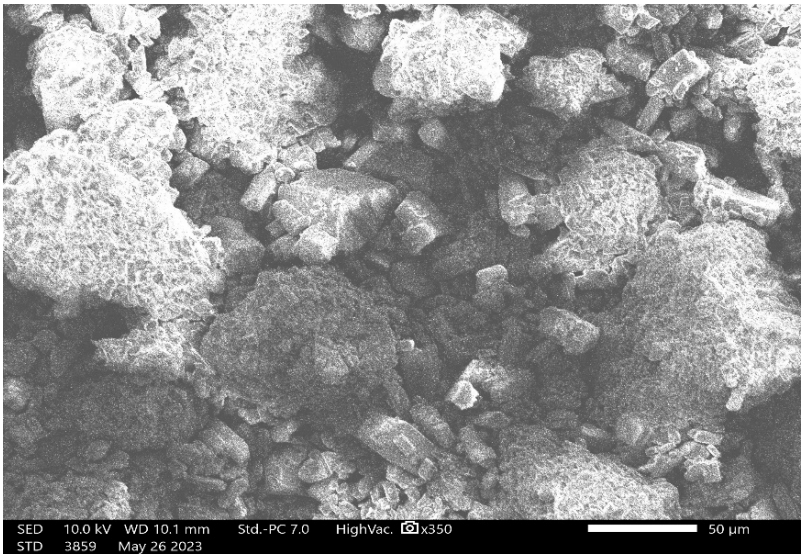

Figure 5. Scanning electron microscope (SEM) image of Li_2CO_3.

The results of this experiment are therefore relevant to the industrial production of lithium carbonate, according to analyses of the chemical makeup of the obtained sample.

4. Conclusion

The solubility level of the components in the sodium carbonate, lithium chloride, and water system was examined using the visual-polythermal method at different temperatures and in a broad range of concentrations. The Li_2CO_3 phase was formed in the system, according to the findings of the study of the Na_2CO_3-LiCl-H_2O system. A significant portion of the polythermal diagram is occupied by the compound's crystallization region, indicating the low solubility of lithium carbonate and the potential for evaporation to separate it from the system's saturated solutions. Future research can use these scientific findings to gain a deeper understanding of the behavior of salts in this system. The results obtained from the system Na_2CO_3-LiCl-H_2O demonstrated the potential to use this system data to develop the production of lithium carbonate in industrial scale.

Author contributions

Bakhodir Abdullayev: Conceptualization, methodology, investigation, writing- original draft; Bakhodir Abdullayev: Visualization, project administration, writing- reviewing and editing; Murodjon Samadiy: Supervision, visualization, project administration, writing- reviewing and editing, reformatting, grammar editing; Dilnoza Axmedova, Jurabek Bozorov, Sarvar Abdiyev, Sanat Samatov, Erkin Yakubov, Khusniddin Botirov, Murodullo Rakhimov, Elbek Mavlanov, Tolmas Olimov, Odil Mamajonov, Mansur Axmedov, Nargisa Shamadinova, Nafisa Ismoilova, Miyasar Zhumanova: Investigation and resource.

Fundings

No fundings

Acknowledgments

The authors would like to thank all those who contributed to this study and worked on its development.

Conflict of interest

The authors declare no conflict of interest.

References

1. Tadesse, B., Makuei, F., Albijanic, B., Dyer, L. The beneficiation of lithium minerals from hard rock ores: A review. Minerals Engineering 2019; 131, 170-184. https://doi.org/10.1016/j.mineng.2018.11.023
2. Wen, H., Liu, Z., Xu, J., Chen, J. P. Nanofiltration membrane for enhancement in lithium recovery from salt-lake brine: A review. Desalination 2024; 591, 117967. https://doi.org/10.1016/j.desal.2024.117967
3. Abdullayev, B., Makhmayorov, J., Ro'ziyeva, Z., Shabarova, U., Deng, T., Samadiy, M. Study of the mutual influence of components in the lithium nitrate–ammonium chloride–water system. New Materials, Compounds and Applications 2023; 7(3), 188-193.
4. Choubey, P.K., Kim, M., Srivastava, R.R., Lee, J., Lee, J.-Y. Advance review on the exploitation of the prominent energy-storage element: Lithium. Part I: From mineral and brine resources. Minerals Engineering 2016; 89, 119-137. https://doi.org/10.1016/j.mineng.2016.01.010
5. Hasan, M. A., Hossain, R., Sahajwalla, V. Critical metals (Lithium and Zinc) recovery from battery waste, ores, brine, and steel dust: A review. Process Safety and Environmental Protection 2023; 178, 976-994. https://doi.org/10.1016/j.psep.2023.08.069
6. Toba, A. L., Nguyen, R. T., Cole, C., Neupane, G., Paranthaman, M.P. US lithium resources from geothermal and extraction feasibility. Resources, Conservation and Recycling 2021; 169, 105514. https://doi.org/10.1016/j.resconrec.2021.105514
7. Wang, J., Hu, H., Wu, K. Extraction of lithium, rubidium and cesium from lithium porcelain stone. Hydrometallurgy 2020; 191, 105233. https://doi.org/10.1016/j.hydromet.2019.105233
8. Balaram, V., Santosh, M., Satyanarayanan, M., Srinivas, N., Gupta, H. Lithium: A review of applications, occurrence, exploration, extraction, recycling, analysis, and environmental impact. Geoscience Frontiers 2024; 15(5), 101868. https://doi.org/10.1016/j.gsf.2024.101868
9. Meng, F., McNeice, J., Zadeh, S.S., Ghahreman, A. Review of lithium production and recovery from minerals, brines, and lithium-ion batteries. Mineral Processing and Extractive Metallurgy Review 2021; 42(2), 123-141. https://doi.org/10.1080/08827508.2019.1668387
10. Swain, B. Recovery and recycling of lithium: A review. Separation and Purification Technology 2017; 172, 388-403. https://doi.org/10.1016/j.seppur.2016.08.031
11. Ettehadi, A., Chuprin, M., Mokhtari, M., Gang, D., Wortman, P., Heydari, E. Geological insights into exploration and extraction of Lithium from oilfield produced-water in the USA: A Review. Energy & Fuels 2024; 38(12), 10517-10541. https://doi.org/10.1021/acs.energyfuels.4c00732
12. Paranthaman, M. P., Li, L., Luo, J., Hoke, T., Ucar, H., Moyer, B. A., Harrison, S. Recovery of lithium from geothermal brine with lithium–aluminum layered double hydroxide chloride sorbents. Environmental science & technology 2017; 51(22), 13481-13486. https://doi.org/10.1021/acs.est.7b03464
13. Song, J. F., Nghiem, L. D., Li, X. M., He, T. Lithium extraction from Chinese salt-lake brines: opportunities, challenges, and future outlook. Environmental Science: Water Research & Technology 2017; 3(4), 593-597. https://doi.org/10.1039/C7EW00020K
14. Talan, D., Huang, Q. A review study of rare Earth, Cobalt, Lithium, and Manganese in Coal-based sources and process development for their recovery. Minerals Engineering 2022; 189, 107897. https://doi.org/10.1016/j.mineng.2022.107897
15. Będowska-Sójka, B., Górka, J. The lithium and oil markets–dependencies and volatility spillovers. Resources Policy 2022; 78, 102901. https://doi.org/10.1016/j.resourpol.2022.102901
16. Zhao, X., Yang, H., Wang, Y., Sha, Z. Review on the electrochemical extraction of lithium from seawater/brine. Journal of Electroanalytical Chemistry 2019; 850, 113389. https://doi.org/10.1016/j.jelechem.2019.113389
17. Xu, X., Wang, Y., Sun, X., Zhou, Y. Vapor–liquid equilibria study of the LiCl+CaCl2+H2O System. ACS omega 2019; 4(2), 4390-4396. https://doi.org/10.1021/acsomega.8b03570