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CCUS: 4443614

CO_2 Mineralization-Enabled Co-Production of Carbonates and Lithium Stable Feed Brines for Direct Lithium Extraction

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Abstract

The successful integration of sustainable, efficient CO_2 utilization with lithium (Li) extraction is crucial to achieving large-scale decarbonization goals. This study presents a novel CO_2-induced pretreatment process that simultaneously produces solid carbonate minerals and Li-stable feed brine, optimized for subsequent direct Li extraction (DLE). This approach addresses the existing research gap in expensive, reagent-intensive brine purification techniques, which result in substantial Li loss in DLE. This process selectively precipitates divalent ions as stable carbonates, attaining permanent CO_2 sequestration with minimal Li loss, and yields treated brine suitable for subsequent DLE. Synthetic brine, representative of a high Mg/Li continental system, interacted with controlled CO_2 flow to induce mineralization under optimized reaction conditions. Process parameters were optimized to enhance carbonate production and ensure Li retention. Hourly collected reacted liquid samples were analyzed using ICP-MS to quantify cation concentration, while post-reaction solid precipitates were characterized using SEM, FTIR, TGA, and XRD to confirm carbonate phase formation. The effects of brine composition, reactive alkalinity, pressure, temperature, and CO_2 flow conditions were investigated to determine the operational window that maximizes divalent cation precipitation and Li stability. Exploratory liquid analyses indicate a significant removal of divalent species (41% of Mg^{2+} and 25% of Ca^{2+}) with minimal loss of Li^{+} (2-4%), verifying the effectiveness of the technology. Additionally, the physicochemical characterization of solid precipitates confirms the presence of $MgCO_3$ and $CaCO_3$. These produced carbonates permanently sequester CO_2 and are also suitable for construction and chemical applications. Moreover, the treated brine exhibits chemical compatibility with all existing DLE technologies, thereby affirming its universal applicability as a pretreatment method. This novel low-carbon technology offers a practical and scalable approach for coordinating carbon utilization and Li extraction, thus contributing to carbon circularity and ensuring resilient Li supply chains for the energy transition.

Introduction

Lithium (Li) is a crucial energy commodity and an essential strategic asset for the transition to a clean-energy economy in the twenty-first century. The accelerated growth of EV and grid-based energy storage businesses causes an acute demand for Li in the battery industry (Dunn et al., 2011; Grosjean et al., 2012). While clays, minerals, seawater, and brines contain trace amounts of Li, continental brines are the most abundant (almost 60% (Wang et al., 2009)) of primary resources, followed by hard rock resources (e.g., spodumene, petalite, and lepidolite). Due to this increasing demand and being 30-50%-less expensive in production than conventional hard-rock sources, the urge for Li recovery from brine has gained the utmost attraction (Tran & Luong, 2015). Hence, the industry is shifting its focus from ores to brines (Grosjean et al., 2012; Kesler et al., 2012; Song et al., 2017).

The current practice of Li extraction from brine using the evaporation pond method is time-consuming and weather-dependent. While several DLE technologies, such as solvent extraction, precipitation, adsorption, and the electrochemical method, have been developed, their performance in continental brines remains severely constrained by high Mg/Li ratios (Mojid et al., 2024; Mojid et al., 2025). Competing divalent ions (i.e., Mg^{2+} and Ca^{2+}), due to their similar ionic radii and charges, exhibit a strong affinity for the sorption sites and thereby lower the Li extraction capacity. Despite the high adsorption capacity and selectivity of Li sorbents, their performance deteriorates markedly in brines with elevated Mg^{2+} and Ca^{2+} concentrations. These competing divalent cations occupy sorption sites, accelerate sorbent degradation, promote co-precipitation, and result in Li losses of 10–20% during chemical-intensive pretreatment.

The identified limitations negatively impact the economic and operational viability of brine-based Li recovery, constituting a significant obstacle to the scaling of DLE technologies. Additionally, existing pretreatment technologies cannot utilize CO_2, thereby missing an opportunity to integrate carbon sequestration with resource recovery. This work presents a CO_2 mineralization-enabled pretreatment framework that selectively removes divalent cations while preserving Li, enabling simultaneous carbon sequestration and the generation of DLE-compatible feed brines. The proposed approach establishes a scalable pathway for integrating CCUS with Li supply chains.

Methods

The process mentioned below selectively precipitates divalent cations as stable carbonate phases, achieving permanent CO_2 sequestration while minimizing Li loss and producing a treated brine suitable for subsequent DLE. The initial pH of the brine, as mentioned in Table 1, was measured as 6.8-7.2. A base blend (pH 13.4) was prepared by mixing 1 N NaOH and 1 N KOH in a 1:1 ratio and adding to the brine at a 1:1 volume ratio to increase alkalinity. The mixture was stirred overnight at 1,500 rpm using a magnetic stirrer, after which the final pH was recorded. This brine-base blend mixture was then preheated in a 3.875 L reactor vessel to the desired temperature (90°C or 120°C) using a thermal jacket for 1 hour. The liquid sample was collected, and the pH was recorded.

Table 1. Chemical composition sampled from West Taijnar Salt Lake in Qinghai, China, with a high Mg/Li ratio (Zhao et al., 2013)

Solution cation	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	Li^{+}	B^{3+}
Content (mg/L)	310	13200	6900	82600	220	180

Once the target temperature was reached, CO_2 gas was injected into the reactor at controlled pressure. CO_2 was first transferred from the cylinder into a transfer vessel at equilibrium pressure, then further pressurized using the ISCO pump in constant-pressure mode. Once the transfer vessel reached the desired setpoint, CO_2 was injected into the reactor by opening the bottom valve, and the reactor pressure was monitored until it stabilized. This process was repeated as needed by refilling the transfer vessel and repressurizing with the ISCO pump. Throughout the procedure, CO_2 bubbling was maintained in the

reactor to ensure a homogeneous reaction. Liquid samples were collected hourly over a 6-hour reaction period, followed by an overnight sample. After completion, the reacted brine was removed, and additional base blend was added to raise pH to ≥ 9.5–10. The solution was reheated to the same temperature, and CO_2 was reinjected following the same procedure. During this second mineralization stage, liquid samples were collected hourly for 4 hours, followed by an overnight follow-up sample. The pH of all samples was recorded. All collected liquid samples, along with the initial brine and brine-base blend, were analyzed by ICP-MS to measure ion concentrations and quantify the effectiveness of selective removal. Moreover, the precipitates were analyzed using FT-IR, TGA, SEM, EDX, and XRD to confirm the presence of $MgCO_3$, $CaCO_3$, and Mg-Ca mixed carbonates.

Results & Discussions

Reacted Liquid Analysis

Figure 1 shows the variation in pH over time under different temperature and pressure conditions. The pH initially rises with the addition of the base and then decreases as CO_2 is injected, as expected. Moreover, when a 1:1 1N NaOH:KOH base blend was used (purple and green curve) rather than 1 N NaOH (black, red, and blue curve), the pH fluctuation became more stable. Stable pH ensures better reaction conditions for carbonate formation. Figure 2 presents the concentration profiles of Mg^{2+} and Ca^{2+}. These preliminary experiments demonstrate a considerable reduction of divalent ions. Specifically, we reduced the Mg^{2+} content by up to 41% and the Ca^{2+} content by 25% in the treated brine. Crucially, Li concentration remained stable during this process, with only a minimal loss of 2% to 4%. This represents a significant improvement over conventional methods, which typically lose 20-30% of the Li. Moreover, fluctuations in Mg and Ca concentrations between 240 and 360 minutes are likely due to continuous CO_2 bubbling, which lowers the system pH, increasing carbonate solubility and favoring the partial redissolution of Mg and Ca from solid phases back into solution.

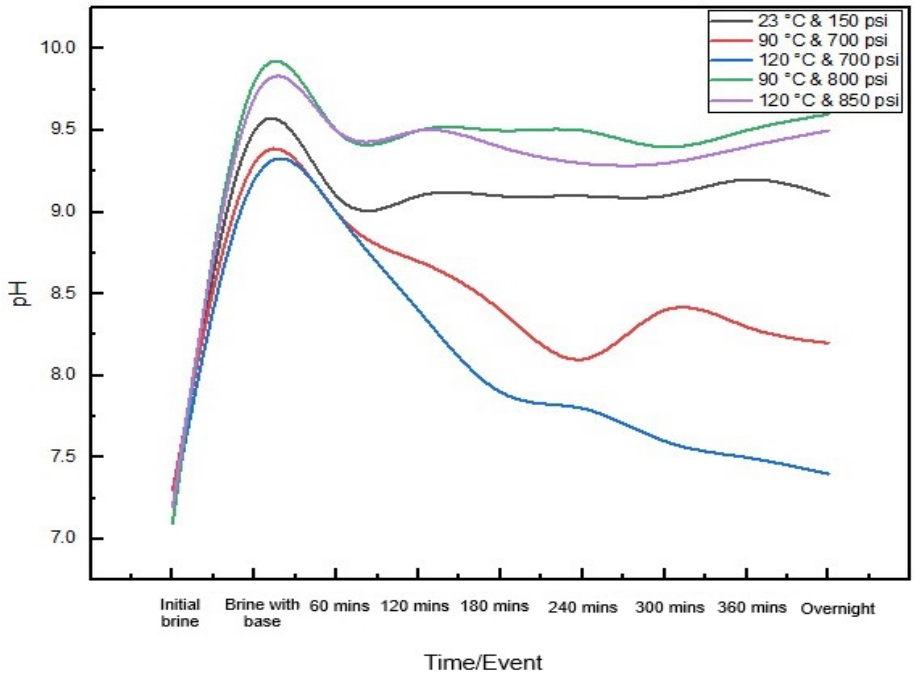
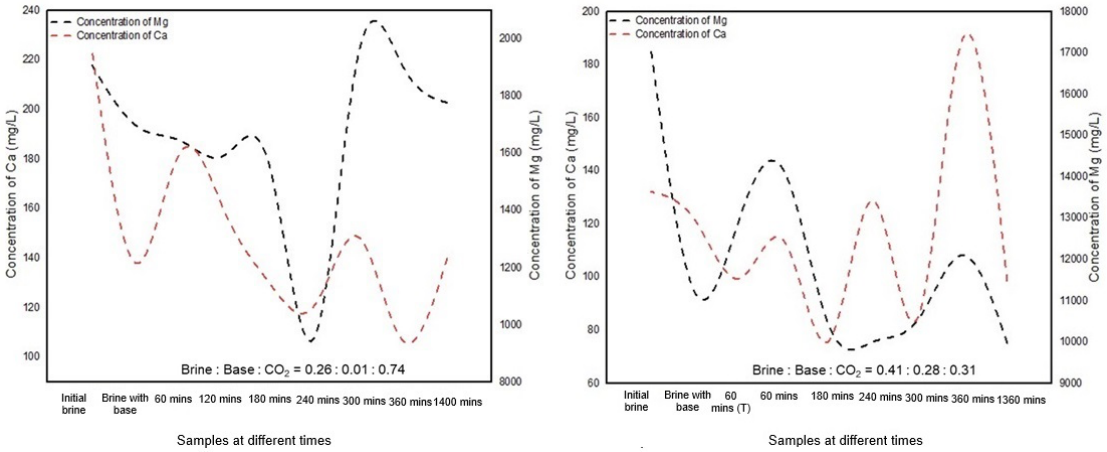


Figure 1. pH variation of liquid samples over time



(a) (b)

Figure 2. Concentration profile of $Mg^{2+}$and Ca^{2+} at (a) 90 °C and 700 psi and (b) 120 °C and 850 psi

Solid Precipitate Characterization

FT-IR plot in Figure 3 shows -OH stretching vibrations of hydroxide groups around 3,400-3,500 cm^{-1} and the peaks around 1,550-1,600 cm^{-1} correspond to the bending vibrations of interlayer water or unreacted free water molecules. This suggests partial hydration and/or surface-adsorbed water. Importantly, the FT-IR spectra demonstrate pronounced absorption features attributed to C–O asymmetric and symmetric stretching vibrations characteristic of carbonate ions, as well as distinct bands near 1,400-1,480 cm^{-1} and 1,100 cm^{-1} confirming the presence of carbonates in the precipitate matrix. Moreover, TGA in Figure 4 reveals a multi-step decomposition profile: an initial weight loss below 200 °C due to physically adsorbed and interlayer water loss between 200-400 °C, followed by progressive dehydroxylation between 400-450 °C and a major mass loss event between 600-900 °C, which is attributable to the decomposition of carbonate phases and corroborates their thermal stability. The residual mass, corresponding to stable oxide formation above 900 °C, further substantiates efficient conversion of aqueous CO_2 to solid carbonates. Collectively, these vibrational and thermal analyses confirm the formation of predominantly magnesite with minor calcite under the studied conditions.

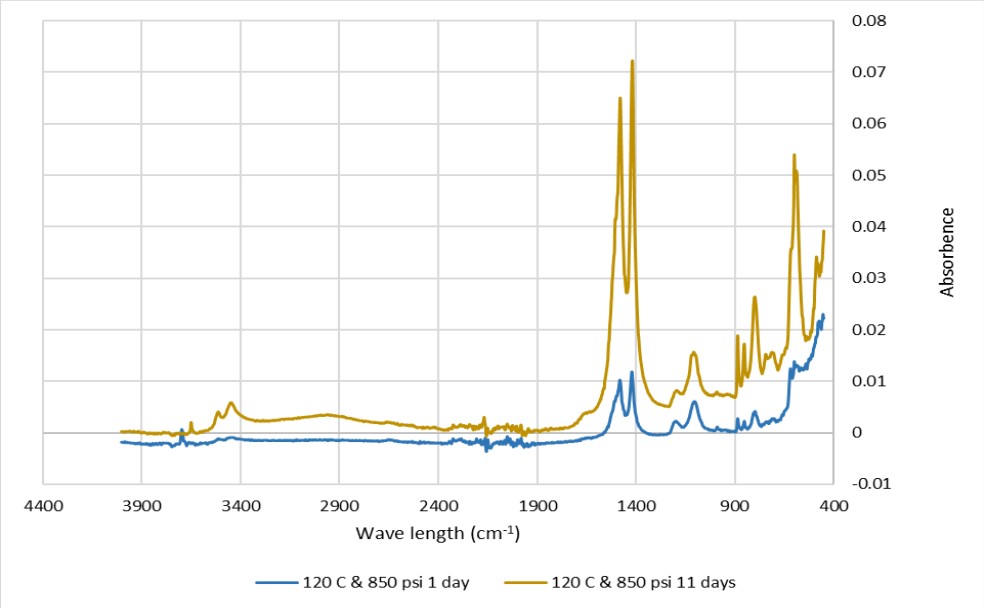


Figure 3. FTIR analysis of the solid precipitate samples

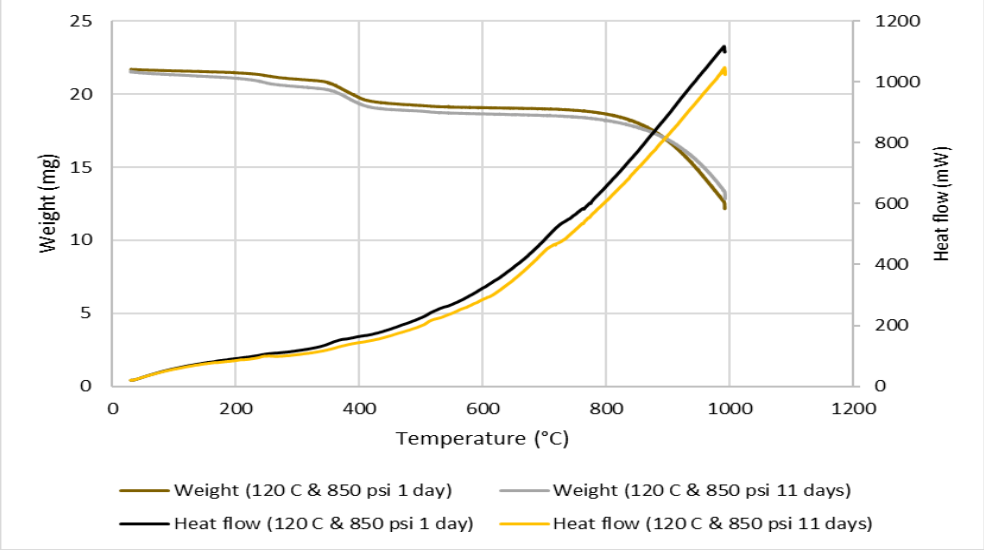


Figure 4. TGA of the solid precipitate samples

Conclusions

Li extraction from brine is the way forward to meet the accelerating demand of the EV industry. Competing divalent cations available in brine occupy sorption sites, accelerate sorbent degradation, promote co-precipitation, and result in Li losses during chemical-intensive pretreatment. Our novel low-carbon technology offers a practical, scalable approach to coordinating carbon utilization and Li extraction, thereby advancing carbon circularity and ensuring resilient Li supply chains for the energy transition.

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