

Application Note 26

Real-time monitoring of ^7Li and ^{23}Na using FlowNMR spectroscopy

Improving extraction efficiency of brines

Introduction

Lithium, the lightest metal in the periodic table, is ubiquitously used across diverse sectors, including glass and ceramics, aerospace, medicine, and nuclear energy. The expanding demand for lithium, propelled by the rapid growth in lithium-ion batteries for electric vehicles and portable electronic devices, has made the effectiveness of its extraction increasingly critical.

Lithium reserves found in salt lake brines account for ~60% of global lithium resources. However, the challenge lies in the efficient separation of lithium ions from co-existing ions like magnesium and sodium in these brines. This has prompted the exploration of new extraction techniques, beyond conventional methods such as adsorption and membrane technologies, which often fall short in their selectivity and sustainability, necessitating resource-intensive subsequent treatments.

Among the innovative approaches, adsorption-coupled electrochemical (ACEC) technology has shown promise in extracting lithium from high-sodium brine with greater efficiency and minimal environmental impact.

FlowNMR spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is an analytical tool for monitoring chemical processes involved in

lithium extraction. The technique's inherent specificity, rich information content, and non-invasive nature make it particularly suitable for

Moreover, recent advances have led to the exploration of lithium-containing brines from deep geological deposits. Initiatives such as those by Cornish Lithium in the UK and Vulcan Energy in Germany represent a significant shift towards tapping into geothermal waters and deep-sea brines. These methods not only expand the potential sources of lithium but also propose a more environmentally benign approach by leveraging the geothermal energy for extraction processes, thereby reducing the carbon footprint associated with lithium mining.



Figure 1 Aerial view of turquoise-coloured pools at Silver Peak Lithium Mine, Nevada, USA

lithium extraction. The technique's inherent specificity, rich information content, and non-invasive nature make it particularly suitable for

real-time monitoring of complex extraction processes. FlowNMR, takes this a step further by enabling continuous monitoring by quantitative, non-invasive analysis under realistic conditions. The reaction mixture from an external reaction vessel is pumped through a flow cell within the NMR spectrometer. This facilitates continuous, representative sampling, allowing high-density data acquisition and real-time multi-nuclear experiments to track dynamic changes occurring during lithium extraction. This is crucial in lithium mining processes, where changes in the concentration of lithium and sodium ions can significantly impact the efficiency and sustainability of the extraction methods.

To our knowledge, this application note demonstrates the first use of FlowNMR spectroscopy for the real-time monitoring and analysis of ^7Li (lithium chloride) and ^{23}Na (sodium chloride) nuclei and quantifying changes in lithium and sodium concentrations, which can provide instant feedback of the efficiency of extraction methods – in particular, lithium extraction from brines. All measurements were performed on an **Oxford Instruments X-Pulse Broadband Benchtop NMR Spectrometer** operating with an external deuterium lock and a probe configured to simultaneously observe ^7Li & ^{23}Na on the Broadband (X-) channel.

FlowNMR setup

The FlowNMR system comprises three main components: the reaction vessel, the flow path, and the NMR flow cell situated within the spectrometer probe (Figure 2). PTFE tubing provides a flow loop from the reaction vessel through the pump and into the flow cell and back out into the vessel. Connections to the reaction vessel were secured using rubber septa to ensure a closed system conducive to continuous flow analysis with all connections using HPLC fittings.

A round-bottom flask, equipped with a rubber septum, was prepared with a solution of 0.5 M

LiCl and 0.5 M NaCl in water, totalling 40 mL. This mixture was circulated through the FlowNMR setup by a peristaltic pump at 2 mL/min.

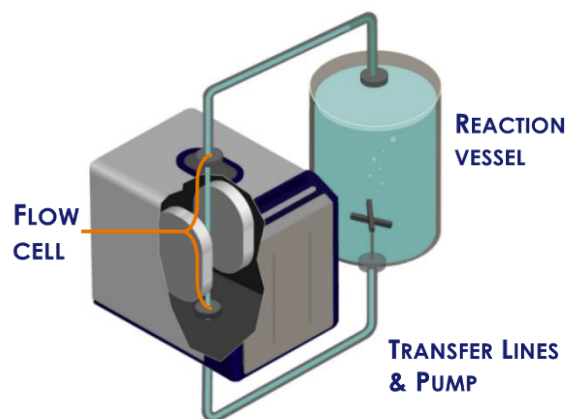


Figure 2 FlowNMR apparatus consisting of a reaction vessel, transfer lines, pump, and Flow Cell (inserted in the probe)

Quantification and Dynamics of Lithium and Sodium

As ^7Li NMR typically displays longer relaxation times than ^{23}Na , quantification of the nuclei is particularly important here to ensure the measurement of precise concentrations. Too short of a relaxation time for Li would result not observing representable concentration of Li whereas, too long would limit the time points that can be observed. This becomes particularly important when sharp changes in concentrations occur. To address this, it is essential to consider that the relaxation delay (RD) should ideally be 5-7 times the T_1 relaxation time to achieve accurate quantification without compromising the frequency of observation. To enable quantitative analysis, this study focused on first measuring the relaxation times (T_1) of ^7Li and ^{23}Na nuclei under flowing conditions (2 mL/min - 4 mL/min) and compared to static relaxation times for a 0.5 M LiCl solution in water. Sodium ions exhibit rapid T_1 relaxation times, ensuring swift data acquisition: at 2 mL/min the effective T_1 time was 49 ms, whereas at 4 mL/min it was 63 ms (Figure 3).

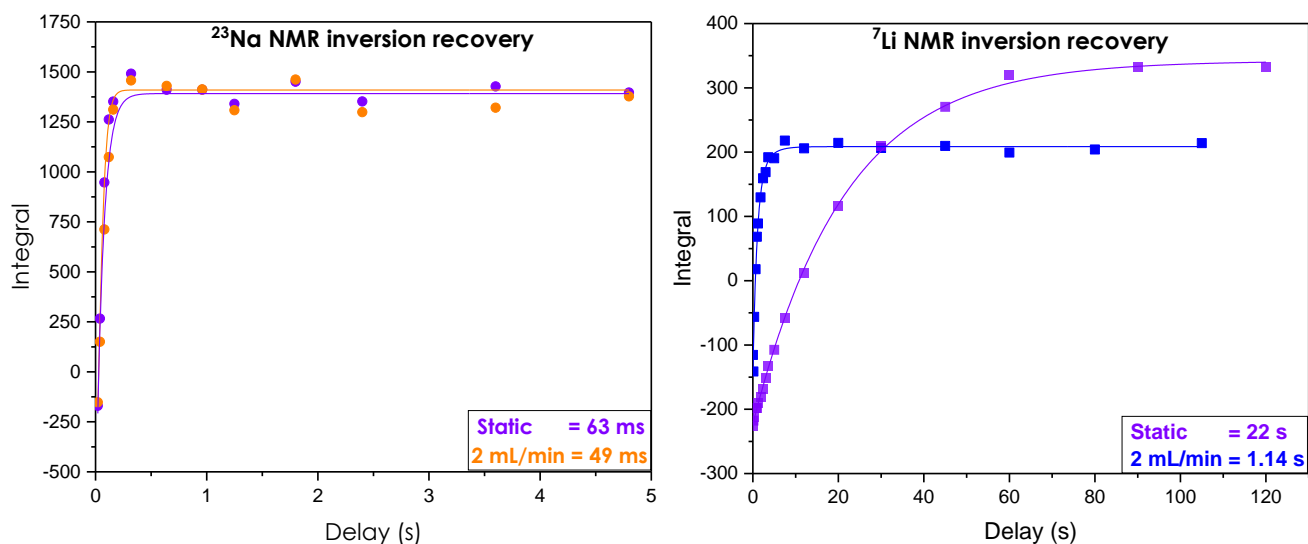


Figure 3 ^{23}Na NMR and ^7Li NMR inversion recovery profiles of NaCl (left) and LiCl (right), recorded static and at 2 mL/min.

Conversely, lithium is characterised by longer T_1 times, posing a challenge for rapid analysis. Our investigations revealed a significant reduction in the effective T_1 relaxation time of lithium, to 1.14 seconds at a flow rate of 2 mL/min which further decreased to 0.63 seconds at 4 mL/min, compared to approximately 22 seconds under static conditions.

These measurements allowed for the optimisation of delay times to approximately 0.5 seconds for ^{23}Na and 6 seconds for ^7Li at a flow rate of 2 mL/min, ensuring quantitative ^7Li , ^{23}Na and ^1H NMR spectra can be collected every eight minutes, facilitating accurate monitoring of the dynamic changes in ion concentrations during the extraction process.

Reaction Monitoring and Data Acquisition

Here we show three reactions, each carried over 6 hours, monitoring the concentration changes when making additions and dilutions of LiCl and NaCl in H_2O . Utilising the T_1 data obtained from inversion recovery experiments, we were able to time interleaved ^7Li , ^{23}Na , and ^1H NMR experiments effectively, with one complete cycle executed every eight minutes.

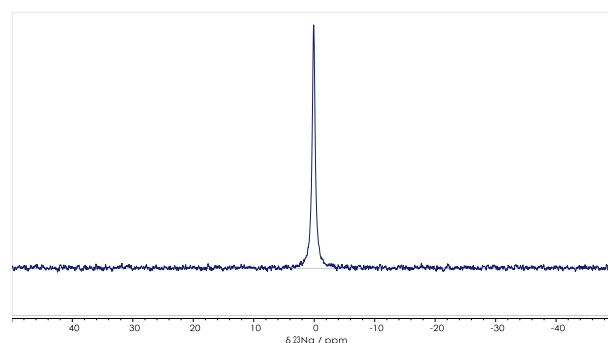


Figure 4 Exemplary ^{23}Na spectrum of NaCl at 2 mL/min

Processing

To effectively correlate NMR spectral data with concentration profiles of the lithium and sodium ions, the NMR data for each nucleus are stacked and aligned, as depicted in Figure 5. This alignment ensures accurate integration of the peaks of interest within the spectra. Following this step, the integration of these aligned peaks yields raw integral values for each spectrum. To account for the flow conditions' impact on these values, a correction factor is applied. This factor is derived by comparing the integrals from static (no flow) spectra to those obtained under flow conditions at corresponding time points. The ratio of static to flow integrals adjusts the raw data, ensuring the measured concentrations accurately reflect the system.

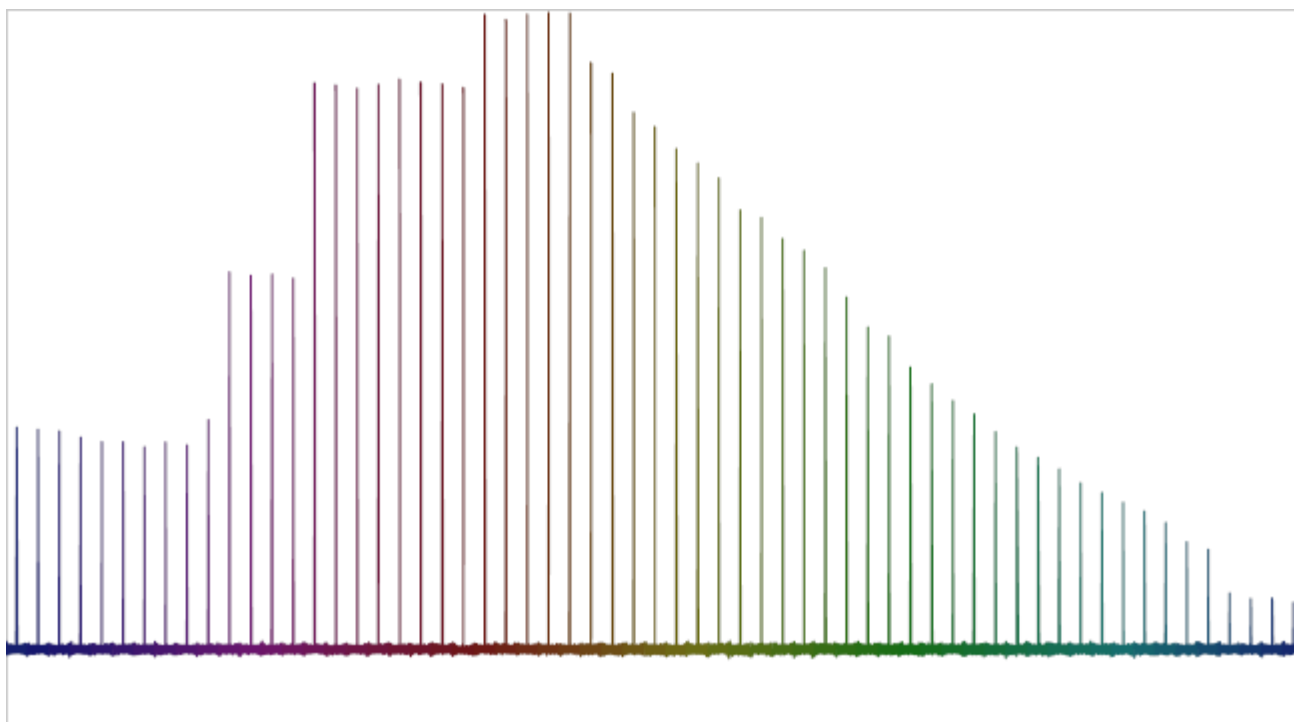


Figure 5 ^7Li NMR horizontal stacked overlay of LiCl at 2mL/min

Using these corrected integrals, the concentrations of lithium and sodium ions are calculated. Given the known initial concentrations of LiCl and NaCl, these corrected integral values allow for the determining the concentration changes over time. This method enables the generation of detailed concentration profiles, plotting the dynamic variations of lithium and sodium levels throughout the extraction process.

Results and discussion

In the first experiment (Figure 6), we observed the behaviour of a system initially balanced at 0.5 M concentrations of both LiCl and NaCl. The concentration of LiCl was then increased to 1 M, creating a disparity in the Li:Na ratio. This adjustment was maintained for 70 minutes, after which the system was diluted, halving the concentrations of both ions. Subsequent adjustments were made to equalise the concentrations of LiCl and NaCl, followed by a simultaneous increase to 1 M at 320 minutes and a gradual decrease back to 0.5 M over the last hour. These manipulations demonstrated the versatility of FlowNMR in tracking concentration changes in real-time,

providing valuable data on the kinetics of ion exchange and solubility dynamics under varying conditions.

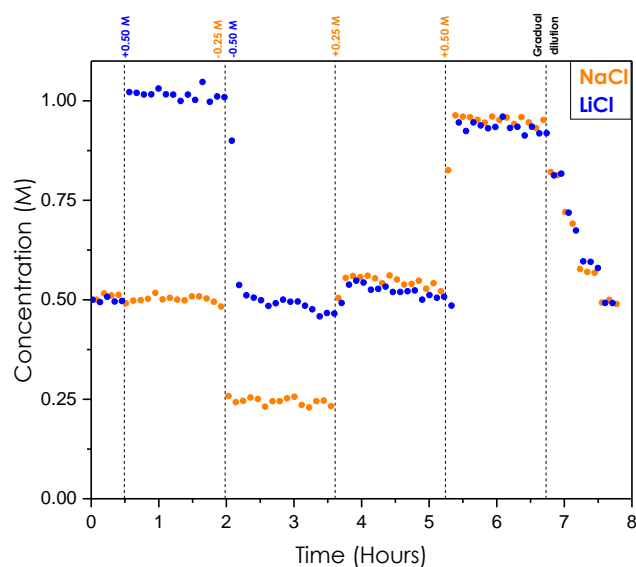


Figure 6 Concentration profile of ^7Li and ^{23}Na FlowNMR monitoring of NaCl and LiCl at 2mL/min

The second experiment further explored the system's response to more pronounced changes in ion concentrations, with a swift increase of LiCl to 1.5 M and subsequent dilution and equilibration steps involving both LiCl and NaCl (Figure 7). This experiment

highlighted the sensitivity of FlowNMR in detecting subtle shifts in ion concentrations, essential for optimising lithium extraction processes.

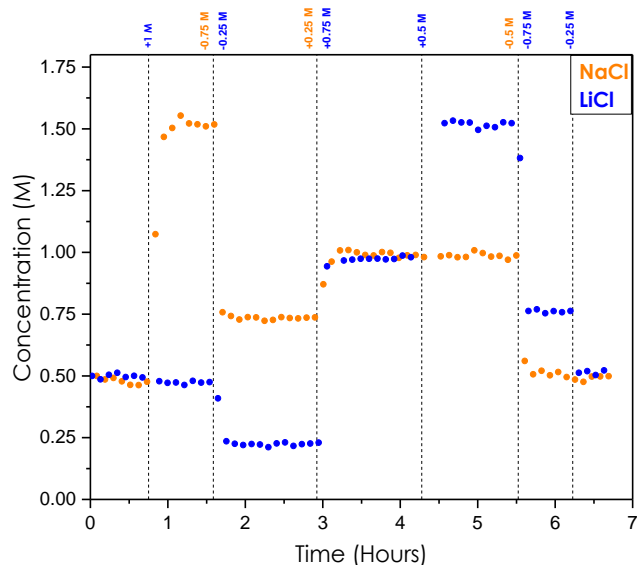


Figure 7 Concentration profile of ${}^7\text{Li}$ and ${}^{23}\text{Na}$ FlowNMR monitoring of NaCl and LiCl at 2ml/min

In the final experiment, a more aggressive modulation of ion concentrations was undertaken, with both LiCl and NaCl concentrations being ramped up incrementally to 1.5 M. To highlight the power of FlowNMR, concentration time plots were able to identify at 180 minutes that the concentration was indeed at 1.5 M, we then used this information to increase the concentration of both LiCl and NaCl to 1.75 M, the reaction system was then methodically decreased over 4 hours to 0 M (Figure 8). This scenario provided a comprehensive view of the system's behaviour across a wide concentration range, showcasing the ability of FlowNMR to monitor the increment decrease of complex reactions and ion interactions effectively.

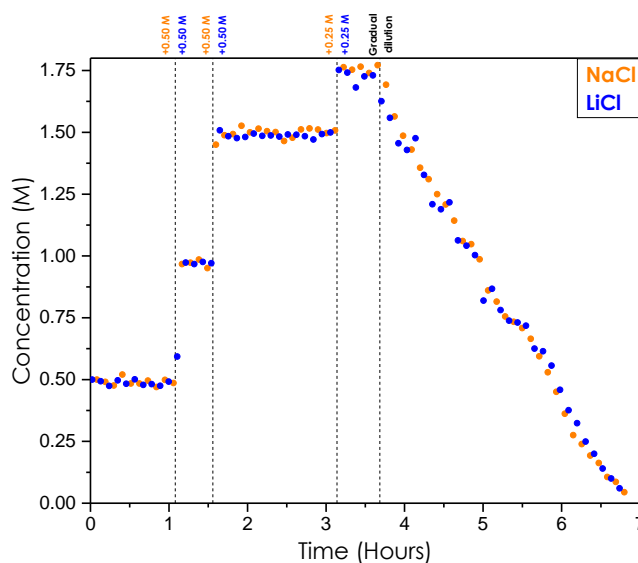


Figure 8 Concentration profile of ${}^7\text{Li}$ and ${}^{23}\text{Na}$ FlowNMR monitoring of NaCl and LiCl at 2ml/min

The technique's high sensitivity in measuring molarity changes, particularly within the millimolar range, facilitates the precise monitoring and optimisation of lithium extraction processes. This precision is essential for producing battery-grade lithium with minimal impurities and is vital for advancing the development of more efficient and sustainable lithium extraction methods. Consequently, this contributes significantly to the enhancement of lithium-ion battery technologies, positioning this technique as a formidable tool. It aids in refining existing extraction methods and supports the development of novel approaches aimed at enhancing the purity and yield of lithium, a crucial component in the battery industry's supply chain. Thus, the technique's relevance and application extend well beyond mere analytical observation, making a substantial contribution to the future of energy storage solutions.

Summary

The series of experiments conducted using FlowNMR spectroscopy have highlighted its significant potential in the realm of lithium extraction. The technique's ability to provide continuous, real-time data on concentration changes offers a profound advantage in studying reaction kinetics, concentration changes, and process optimisation. The experiments highlighted not only the versatility and sensitivity of FlowNMR, using the **Oxford Instruments X-Pulse Broadband Benchtop NMR Spectrometer** operating with an external deuterium lock, but also its applicability in addressing real-world challenges in lithium extraction processes



If you have any questions about this application note, please contact our experts: magres@oxinst.com

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