Early-stage lithium recovery from EV battery black mass by CO_2 in pilot scale

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The green transition focusing on developing a more sustainable and environmentally friendly economy is nowadays becoming indispensable on a global basis due to the climate crisis. In fact, stricter regulations provided by the European Commission on the use of internal combustion engine vehicles, which contribute to greenhouse gas emissions have boosted awareness of electric vehicles, thereby sharply increasing the demand of lithium-ion batteries (LIBs). To provide a circular economy and ensure a sustainable battery lifecycle, the EU Battery Regulation (European Union 7/28/2023) is covering different aspects of the complete value battery chain such as recovery rates, metal recovery rates, extended producer responsibility, batteries classification and consumer information. Owing to these legal requirements one of the main priorities and challenges for the battery industry is to achieve certain recycling rates of critical and strategic materials, e.g. 80 % lithium by 2032. Therefore, the challenge of the scientific community in recent years has been to develop breakthrough technologies for lithium recovery which are cost-efficient and at the same time aligned with the planetary boundaries. In response to this, research into the early-stage recovery of lithium has increased significantly in recent years, as lithium is usually recovered at the end of the recycling process, which results in higher yield losses.

One of the most promising approaches is the use of CO_2 for the recovery of lithium from the black mass of end-of-life batteries because consuming CO_2 helps to mitigate greenhouse gas emissions by converting waste into valuable materials as well as reducing the energy required for lithium extraction. This carbonation process can be carried out by using different approaches and operational parameters for producing Li_2CO_3, which can be used in the production of new batteries, contributing to a circular economy. Laboratory-scale tests under atmospheric pressure, in which CO_2 gas is continuously fed into the aqueous black mass suspension, achieve an extraction of up to 97 % at a phase ratio of 10 g/l and a CO_2 flow rate of 6 l/min. (Milicevic Neumann et al. 2024) Adding the supercritical CO_2 state the so-called COOL-Process, which is patented by the TU Bergakademie Freiberg, is employed. (Bertau et al. 2017) Using a temperature of 230 °C, 100 bar and a solid-liquid (S/L) ratio of 120, lithium recoveries of 99 % have been reported in lab-scale with a co-mobilization of other metals of < 3 %. (Pavón et al. 2021)

Currently, this process is being validated in a pilot plant (TRL 5) placed at the Fraunhofer IKTS facilities (Freiberg, Germany). Although the development of the COOL process was not only intended for the recovery of lithium from secondary material but also from primary material and thus offering a holistic solution that regardless of the input material the product obtained is battery grade lithium carbonate, the question here is whether the use of supercritical conditions is necessary to offer not only a sustainable but also a cost-effective alternative. Therefore, the current work focuses mainly on the comparison of different procedures and methods using CO_2 for early-stage lithium recovery in pilot plant scale to identify not only the one that provides the highest recovery rate but also selectivity, potential for industrial implementation, and of course economic and environmental considerations.

Pyrolyzed black mass provided by Treibacher Industrie AG (Carinthia, Austria) was characterized by ICP-OES (ICAP PRO X ICP-OES, Thermo Fisher Scientific Inc., USA) after a digestion with HNO_3/HCl mixture (3:1) performed using a Multiwave7000 microwave (Anton Paar GmbH, Austria). Lithium extraction from black mass was carried out using a stainless-steel autoclave reactor with a technical effective volume of 200 l (Sigmar Mothes Hochdrucktechnik GmbH, Germany). The powdered samples were mixed in 120 l of deionized water at desired (l/s) ratios. The reactor was flushed with CO_2 to remove the air and the suspension was then heated up to 230 °C (reaction temperature) and the CO_2 pressure was adjusted to the investigated values (20 - 100 bar). After a reaction time of 2 - 4 hours, the reaction was stopped by actively cooling of the reactor. When the suspension reached

ambient temperature, the mixture was filtered in two steps using first an eight-chamber filter press (type SMM1-150S, Simex Vertrieb GmbH & Co. KG, Germany) and a membrane filter (PP/EPDM, 0.2 µm; Wolftechnik Filtersysteme GmbH & Co. KG, Germany). The resulting leachate was analyzed using ICP-OES to assess lithium leaching efficiency. To produce Li_2CO_3, the particle-free leach solution was first concentrated gradually through evaporation in a heatable 20 l stirred reactor (Pfauder Normag Systems GmbH, Germany), reducing the volume by 90 %. The crude salt was separated through hot filtration and further purified. The product's purity was determined via ICP-OES after dilution in a 0.32 M HNO_3 solution.

Regardless the different operational conditions used (pressure, reaction time) in pilot scale, the extraction of lithium was > 85 % (Figure 1b). To reach almost the full extraction of such critical raw material (> 98 %), the reaction time had to be increased from 2 - 4 hrs. In addition, co-mobilization of other metals, especially Al and Mn, was observed. However, even with the COOL process as a whole, this is not a drawback since the CO_2 leaching is followed by a membrane separation step - electrodialysis - in which these non-monovalent metals remain in the diluate while only lithium is present in the concentrated solution.

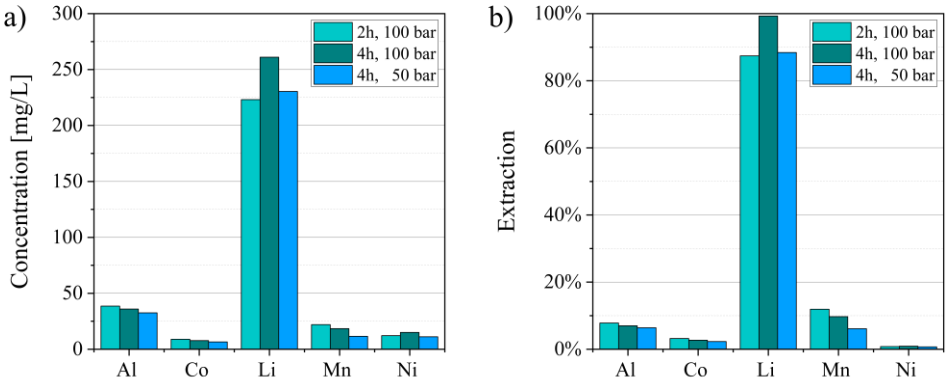

Figure 1: a) Influence of reaction time and CO_2 pressure on metal concentration. b) Extraction efficiency in the COOL process at pilot scale (200 l reactor); l/s = 120, T=230°C, stirring: 250 rpm

It has been therefore demonstrated that supercritical conditions are not required for an effective Li extraction since using 50 bars in the digestion step with CO_2, 88 % of Li was obtained. Thus, these findings are promising for an improvement in the cost-efficiency of the process, where the balance between Li extraction and costs is the key. Further tests were carried out in the pressure range 0 - 100 bar and l/s ratios of 10 - 120 for evaluating the optimal operational conditions which allows an industrial feasibility implementation of the process.

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