Efficient Lithium Recovery from End-of-Life Batteries in Pyrometallurgical Recycling Processes by Early-Stage Separation from Black Mass

Christin Stallmeister and Bernd Friedrich

Abstract

Due to increasing electrification and therefore demand for battery raw materials, their recovery from secondary sources like spent lithium-ion batteries is highly important. One process option is a pyrometallurgical route to enrich cobalt, nickel, and copper in an alloy. In current industrial smelting processes, the contained lithium and aluminum are transferred to the slag phase and are difficult to recover. But especially the recycling of the critical metal lithium will be crucial in the future, also to meet legal requirements. Processing the slag regarding lithium recovery has different drawbacks, such as energy-intensive slow cooling for targeted phase formation and milling, as well as chemical-consuming leaching operations. In literature, approaches for lithium collection in the flue dust are reported as well, but require high temperatures of up to 1800 °C. Alternatively, this study investigates the influence and benefits of an early-stage lithium separation before entering the smelting process with black mass. Therefore, shredded battery material was thermally conditioned under an inert atmosphere at 630 °C. During the thermal treatment, the organic content is removed and the contained lithium is transferred to water-soluble compounds. Afterward, 55% of lithium was selectively recovered by water leaching. Suitable slag systems for smelting lithium-depleted black mass were investigated by FactSage calculations, and experimental implementation resulted in the recovery of 99% Cu, 91% Co, and 93% Ni in the metal phase. Thus, the competitiveness of a combination of early and water-based lithium recovery and pyrometallurgical smelting operation against the lithium recovery from slag or flue dust was proven.

Keywords

Lithium-ion battery · Recycling · Pyrometallurgy · Smelting · Lithium

1 Introduction

Recycling of spent lithium-ion batteries (LIBs) is of high importance against the background of ongoing electrification of society, especially in the transport sector. NMC battery raw material demands and prices for the critical elements Ni, Co, graphite, and Li are increasing accordingly [1, 2]. To be able to cover demand while avoiding dependence of mining countries, meet legal requirements of the EU [3, 4], and contribute to a circular economy, establishing efficient recycling processes for spent LIBs is necessary. Therefore, various approaches by different combinations of thermal, mechanical, and hydro- or pyrometallurgical process steps are carried out in research and industry [5–7]. The advantage of pyrometallurgical recycling processes is their robustness to fluctuating input flows [5]. Against the background of varying cell chemistries, this represents a strength compared to hydrometallurgical process routes [5]. Pyrometallurgical smelting operations are suitable as splitting operations for the concentration of Cu, Co, and Ni in an alloy and slagging or evaporation of elements like Al, F, and Li [8]. In

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C. Stallmeister (✉) · B. Friedrich
Institute of Process Metallurgy and Metal Recycling (IME), RWTH Aachen University, Aachen, Germany
e-mail: cstallmeister@ime-aachen.de

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the past, focus was on recovering the more monetarily valuable elements Co, Ni, and Cu [7]. However, now that Li has been classified as a critical element [9] and it will be indispensable for battery production in the future [6], its sufficient recovery is necessary.

In common pyrometallurgical recycling processes, Li is either enriched in the slag or flue dust. These two approaches were already investigated in literature [10–16]. Input feed for smelting trials can be whole batteries resp. shredded LIBs or thermally treated and/or separated black mass [5]. Melting of black mass offers the advantage of previous aluminum and copper foil recovery, resulting in lower slag volumes.

In a previous comparative study by the authors [17], a whole battery shredder was melted in an electric-arc furnace with CaO and SiO_2 addition for Li slagging. Around 71.9% of Li was enriched in the slag by adding 350 g fluxes per 1 kg LIBs shredder. The approach of Li enrichment in $LiAlO_2$ phases in the slag by slag engineering, including slow cooling, is carried out in current research projects [18]. The aim is to subsequently concentrate Li-rich aluminate phases by flotation before entering hydrometallurgical processing. A high Al share of the input feed is necessary for this approach.

In comparison, Sommerfeld et al. [14] achieved a Li slagging of 82.4% by smelting pyrolyzed black mass with 200 g SiO_2 addition per 1 kg black mass, resulting in a SiO_2-Al_2O_3-Li_2O based slag system. A comparative study by Sommerfeld et al. [13] on the volatilization of Li was carried out with CaO addition. By adding 130 g CaO per 1 kg of black mass, 80.4% of Li-input was evaporated at 1800 °C. Another approach is applying the concept of an InduRed reactor for pyrometallurgical LIBs recycling and Li evaporation in a study by Holzer et al. [19]. They removed around 92% of Li from Al and F-free, NMC cathode material without flux addition at around 1550 °C. However, a previous study [15] has shown that in case of spent and Al containing black mass, a lower Li removal of 75% can be achieved with this approach. Some other studies have been conducted on the accumulation of Li in flue dust in dependence of input material composition, especially Al content. For example, Hu et al. [12] describe Li transfer of up to 68.3% in the flue dust in the form of Li_2CO_3. Georgi-Maschler et al. [10] used an Al-containing black mass as feed material, resulting in a transfer of 68.6% of Li-input in the flue dust at temperatures between 1700 and 1750 °C.

The two approaches described for the enrichment of Li in the slag or in the flue dust each have disadvantages. The selectivity of enrichment in either phase depends on the composition of the input feed and fluxes. In all of the described cases, a complete enrichment in one single phase is not possible. Moreover, slag and flue dust are intermediate products and require subsequent processing for Li recovery. In the case of the slag, this means energy-intensive mechanical processing and acidic leaching or chlorination roasting [20]. For SiO_2-based slag systems, leaching is challenging due to silica gel formation and requires high acid concentrations [21]. Additional chemicals such as Na_2CO_3 are added for Li precipitation [21] so that wastewater with a high salt load is produced. Environmental issues caused by leach-residues are also to be taken into account [5].

The second option of Li enrichment in flue dust requires high process temperatures of up to 1800 °C. The flue dust itself needs to be purified, for which different approaches, depending on the composition, are reported in literature. A leaching efficiency of ~90% is reported for sulfuric acid leaching [10], and up to 63.3% of Li salt was recovered by carbonated water leaching [12] in a different study from the flue dust. Multi-stage Li recovery can therefore lead to Li losses in the single process steps.

An alternative for recovering Li is the concept of early-stage lithium recovery (ESLR), reported in previous studies [22–25]. The present study investigates the adoption of this concept for the pyrometallurgical recycling process of spent LIBs with special regard to Li recovery for the first time.

Early-Stage Lithium Recovery The ESLR concept is based on a two-stage process consisting of a thermal pre-treatment and water leaching of Li. Whole or shredded batteries, as well as separated black mass, can be used as input feed for thermal treatment. The difference between those two input fractions lies mainly in the metal content of Fe, Al, and Cu, since the battery casing and current collector foils are already separated in the case of black mass [5]. The black mass itself is a powder mixture of the Li containing NMC oxides, graphite and organic residues from binder and electrolyte as well as small Cu and Al particles [26].

Previous studies have found temperatures between 600 and 750 °C optimal for the heating process [22, 27, 28]. During thermal treatment, the organic content, i.e., binder, electrolyte, and separator, is removed from the battery material and the contained metal oxides are (partly) reduced [22, 24, 29, 30]. To create reducing conditions during the process, an inert atmosphere, e.g., under N_2 or Ar, is beneficial compared to mixtures with O_2 [22, 27, 28]. The mixed Li-containing metal oxides are partly reduced, for example, to Ni, NiO, MnO, and CoO in case of NMC batteries [22, 28, 29]. A further reaction product is Li_2CO_3 (see Eqs. (1), (2), (3) adapted from [16, 29]), which has a water solubility of 13.3 g/L at 20 °C [31].

$$4LiMeO_2\,(s) + C\,(s) \rightarrow 2Li_2O\,(s) + 4MeO\,(s) + CO_2(g) \quad (1)$$

$$Li_2O\,(s) + CO_2\,(g) \rightarrow Li_2CO_3(s) \quad (2)$$

$$2LiMeO_2\,(s) + 3CO\,(g) \rightarrow Li_2CO_3 + 2Me\,(s) + 2CO_2(g) \quad (3)$$

The second step of ESLR is based on this Li_2CO_3 formation. Selective recovery of produced Li_2CO_3 is carried out by water leaching of the black mass fraction. Since the other black mass components, except parts of Al and F [22, 27, 28], are not water soluble under the given conditions in significant values, a Li salt with a purity >92% [24, 28] can be recovered by water evaporation. The advantage of this approach is that no chemicals are used, and it can be integrated into existing process routes for battery recycling. The whole concept is currently under intensive research. Until now, Li recovery yields between 55% and 70% [22, 27, 28, 32] are reported for spent NMC LIBs material. Improvements of the thermal treatment step and of the leaching, e.g. by CO_2 injection [33, 34], promise further improvement of Li recovery.

In the frame of pyrometallurgical LIBs recycling, integration of ESLR has the potential to lower process temperatures of smelting operations as Li volatilization becomes obsolete and to avoid energy- and chemical-intensive slag processing for Li recovery. The present study is the first to investigate the ESLR process steps in combination with a pyrometallurgical black mass smelting process experimentally.

2 Materials and Methods

To recover the valuable metals, and especially Li, from NMC black mass, the ESLR process was carried out before the smelting operation. Therefore, an NMC 622 black mass, generated by an inert industrially shredder process and subsequent sieving, was first pyrolyzed and second water leached for Li recovery. The Li-depleted black mass was smelted with flux and CuO addition for sufficient carbon usage and separation of a Cu, Co, and Ni alloy from a slag phase. The general process scheme is presented in Fig. 1, and the single process steps are described in detail below.

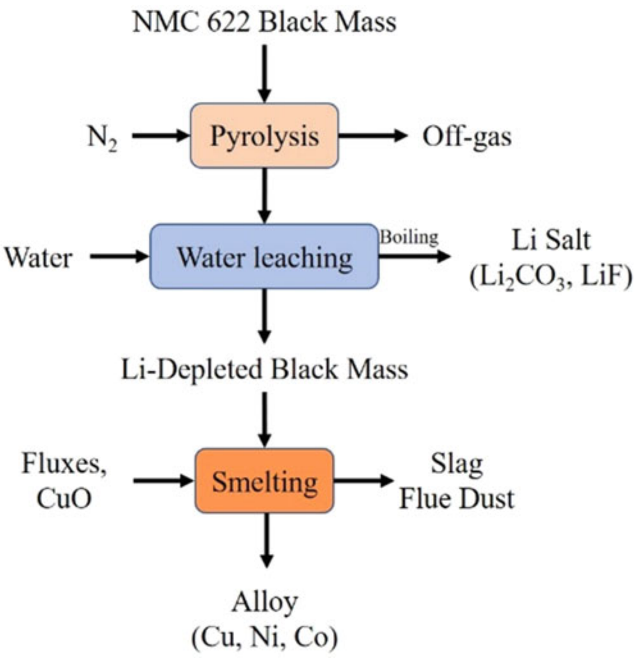
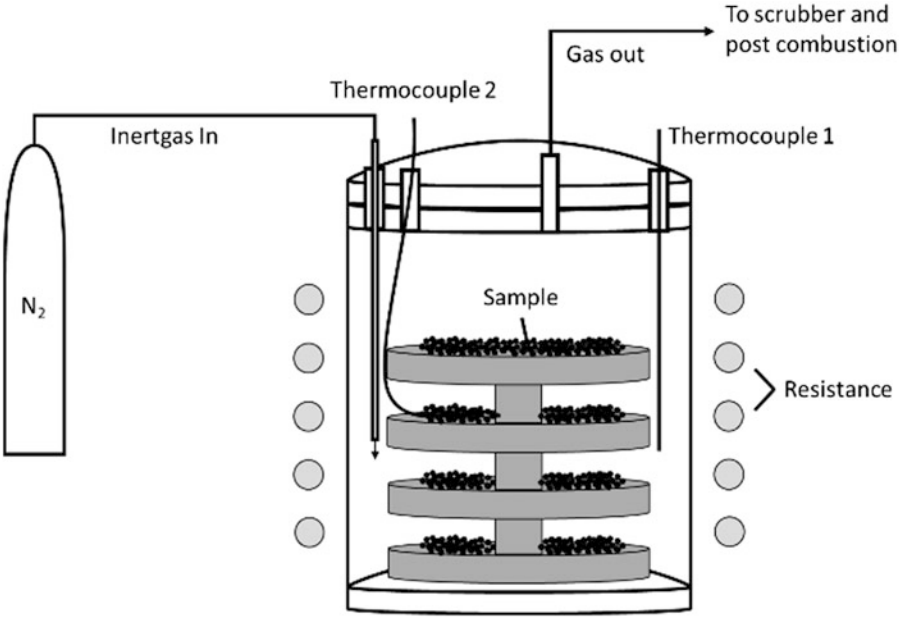


Fig. 1 Process flow chart of the present study

Fig. 2 Setup of pyrolysis trials



2.1 Black Mass Preparation by ESLR

Table 1 gives the initial black mass composition used for the trials. Analysis was carried out by combustion method (ELTRA CS 2000, ELTRA GmbH, Haan, Germany), ICP-OES (Spectro CIROS Vision, Spectro Analytical Instruments GmbH, Kleve, Germany), and ion chromatography (811 Compact IC pro, Deutsche Metrohm GmbH & Co. KG, Filderstadt, Germany). The maximum size fraction determined by sieving is 0.5 mm.

Thermal treatment of 4.8 kg of the Li-depleted black mass was carried out in two batches in a resistance-heated furnace, equipped with a steel chamber with water cooled lid. The setup is shown schematically in Fig. 2. For homogeneous heat treatment, the material was divided into four steel shells per trial, stacked on top of each other with spacers. The process parameters for the thermal treatment were chosen based on the best-case scenario of a previous study [22]. The furnace was heated with 300 °C/h to 630–650 °C in the material under constant 14 l/min N_2 flow. The targeted material temperature was maintained for 90 min. After the pyrolysis process, the LIBs material was cooled down in the furnace under inert atmosphere. Generated organic and F containing off-gas was treated in a two-step scrubber filled with NaOH and water before entering thermal post combustion.

After the pyrolysis, black masses from the two batches were mixed and water leached. The leaching parameters were set based on a previous study [22], but in larger scale:

- Solid to liquid ratio of 1:25
- 90 min stirring with 300 rpm
- 3 and 5 L scale
- Water washing of filter cake with 500 ml

After leaching, the solid residue was filtered, water washed, and dried for 24 h at 80 °C. The solution was analyzed for Li content by ion-selective electrode measurement (DX207 Li ISE, Mettler-Toledo GmbH, Gießen, Germany). Table 1 gives the resulting composition of the dried, Li-depleted black mass.

2.2 Thermochemical Calculation and Smelting Trials

Thermochemical modelling of the smelting trials was carried out with the Equilib module of FactSage™ 8.0 [35]. The FactPS, FToxide, and SGTEb database were used for the calculations. Because the black mass contains Al, which will be transferred to the slag phase and favors Li slagging as well, possible slag systems with high Li solubility were chosen for the smelting trials.

Table 1 Initial and Li-depleted, elemental black mass composition

Element	Al	Cu	Co	Li	Mn	Ni	P	C	F
Initial BM (wt.-%)	2.02	1.83	5.30	3.21	5.09	14.60	0.55	39.90	2.50
Li-depleted BM (wt.-%)	2.31	2.27	5.97	1.84	5.59	16.60	0.58	46.00	2.56

This also allows working at lower temperatures than volatilization operations, and certain Li contents in slags are advantageous for their use in the cement industry [36]. At the same time, the slags should have lowest possible solubility for the other valuable metals Cu, Co, and Ni, as well as low liquidus temperature < 1500 °C with low flux addition. As fluxing agents, CaO and SiO_2 were considered.

The smelting trials were carried out in a resistance-heated furnace. Sixty gram of black mass per trial was mixed with fluxes and minimum 145 g of CuO as a dummy material for graphite consumption, similar to Sommerfeld et al. [13, 14] and a previous study by the authors [17]. The purity of used SiO_2 was >99.998%, and for CaO, it was >94.5%. The CuO had a purity >98.9%. Afterward, the material was placed in an alumina crucible in the furnace, heated with 350 °C/h up to 1500 °C. After reaching the target temperature, a further CuO addition was carried out depending on the melting behavior and visually detectable graphite content. After the last CuO addition, a 20 min holding time was carried out for complete reaction and metal settling. Then, the power of the furnace was turned off, and the material cooled down in the furnace.

For metal and slag separation, the crucible was cracked for manual separation of the product phases. The metal phase was polished and analyzed by spark spectrometer measurement (SPECTRO MAXx, Spectro Analytical Instruments GmbH, Kleve, Germany). Slag analysis was carried out after grinding by ICP-OES, combustion, and ion-selective electrode (F-measurement).

3 Results

This section presents the results of the experiments and thermochemical modelling. A mass balance based on chemical analysis is carried out for each process step and is summarized for the whole process chain.

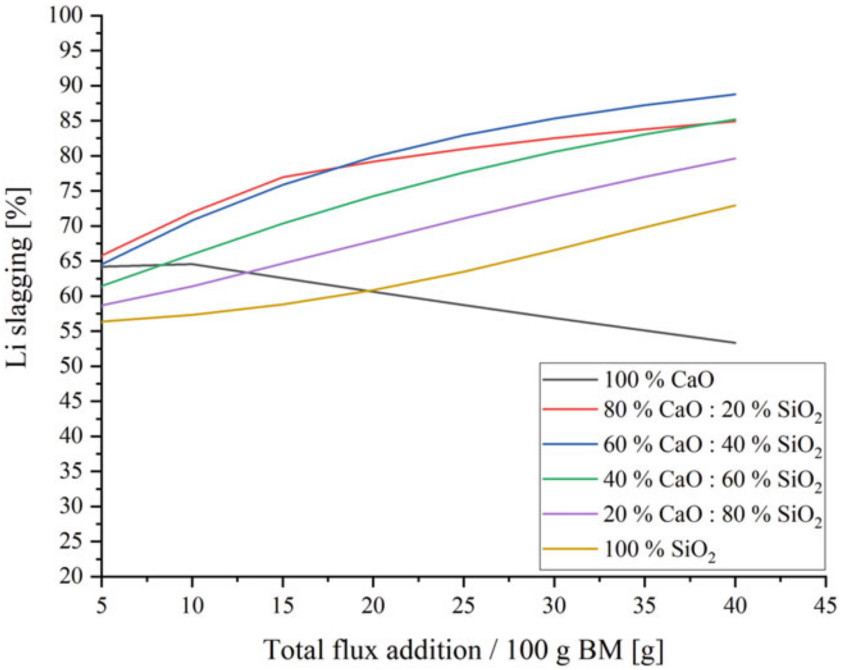
3.1 Results of ESLR Process

During the thermal treatment trials, an organic and F containing off-gas is produced. FTIR analysis of this off-gas was already carried out for small-scale experiments. Therefore, the main off-gas components are known to be residual electrolyte components and CO, CO_2, and organic cracking products such as CH_4 and further alkane. Parts of F are removed by formation of HF and fluorinated hydrocarbons. The organic and partly fluorine removal resulted in an average mass loss of 11.8% for the two trials.

Water leaching of the black mass lead to a second decrease in mass due to Li removal. The Li_2CO_3 formed during thermal treatment under reducing conditions is dissolved from the black mass. In addition, small amounts of LiF are dissolved as well. This results in an average mass loss of the black mass of 9.1% during the leaching trials. Therefore, the overall mass loss of the initial black mass over the ESLR process amounts to 19.8%. Calculation of the leaching efficiency (LE) of Li was carried out in two ways, presented in Eqs. (4) and (5), based on mass loss and related to black mass compositions from Table 1 and Li analysis in solution by ion-selective electrode. The results of the calculations show a good agreement with 54.0% and 55.4% despite different analysis methods.

$$\mathrm{LE\ (Li)} = 100\% - \frac{m_{\mathrm{Li-depleted\ BM}} \cdot c\ (\mathrm{Li})_{\mathrm{Li-depleted\ BM}}}{m_{\mathrm{initial\ BM}} \cdot c\ (\mathrm{Li})_{\mathrm{initial\ BM}}} * 100\% = 54.0\% \tag{4}$$

Fig. 3 Calculated Li-slagging and Li share in slag in dependence of total flux addition and SiO_2: CaO ratio at 1500 °C



$$\mathrm{LE}\ (\mathrm{Li}) = \frac{V_{\mathrm{Solution}} \cdot c\ (\mathrm{Li})_{\mathrm{Li\ solution}}}{V_{\mathrm{Solution}} \cdot \mathrm{c}\ (\mathrm{Li})_{\mathrm{solution}} + m_{\mathrm{Li-depleted\ BM}} \cdot c\ (\mathrm{Li})_{\mathrm{Li-depleted\ BM}}} * 100\% = 55.4\% \tag{5}$$

The detailed investigation of the ESLR process is under intensive research and addressed in various studies, so reference is made to literature, e.g., [22–25, 27–29, 37, 38], for more in-depth explanations.

3.2 Results of Thermochemical Calculations

FactSage™ 8.0 [35] calculations on Li slagging were performed to select slag-systems to be investigated in experiments. Different total flux amounts of SiO_2 and CaO and their ratios to each other were considered at 1500 °C. The results are presented in Fig. 3. Although most of the slags have a liquidus temperature < 1200 °C, a process temperature of 1500 °C is chosen in case alloys with lower Cu content are produced in the future. This will be relevant if Ni-rich co-feeds are considered or graphite is removed before entering the smelting process, e.g., by flotation. CuO addition in this study is to be regarded as a dummy.

All considered slag systems show significant slagging of Li. Except of the system with 100% CaO addition, Li slagging rises with rising slag volume. For sustainable process design and to keep losses of Co, Ni, and Cu minimal, the smallest possible total flux additions are to be chosen for the melting trials. Therefore, addition of 15 g/100 g black mass is chosen for the three CaO:SiO_2 ratios with highest Li slagging (40–80% CaO). An additional trial is carried out with 20 g/100 g black mass addition for the 40% CaO: 60% SiO_2 ratio.

3.3 Results of Smelting Trials

A metal and slag phase were recovered in all trials, but in the trials with highest CaO share as well as in the trial with a total flux amount of 20 g/100 g black mass, a third, powder phase remained. Exemplary pictures of the three phases are presented in Fig. 4, and Table 2 gives the mass distribution of the trials.

Table 2 Input feed and mass of generated product phases of the conducted trials in g

Trial	BM	CuO	SiO_2	CaO	Metal	Slag	Powder
S1	60	145	5.4	3.6	130.2	19.0	–
S2	60	180	3.6	5.4	156.6	23.1	–
S3	60	165	1.8	7.2	124.4	22.0	20.6
S4	60	145	7.2	4.8	79.9	2.4	54.9

Fig. 4 Exemplary pictures of left: metal; middle: slag; right: powder with metal droplets

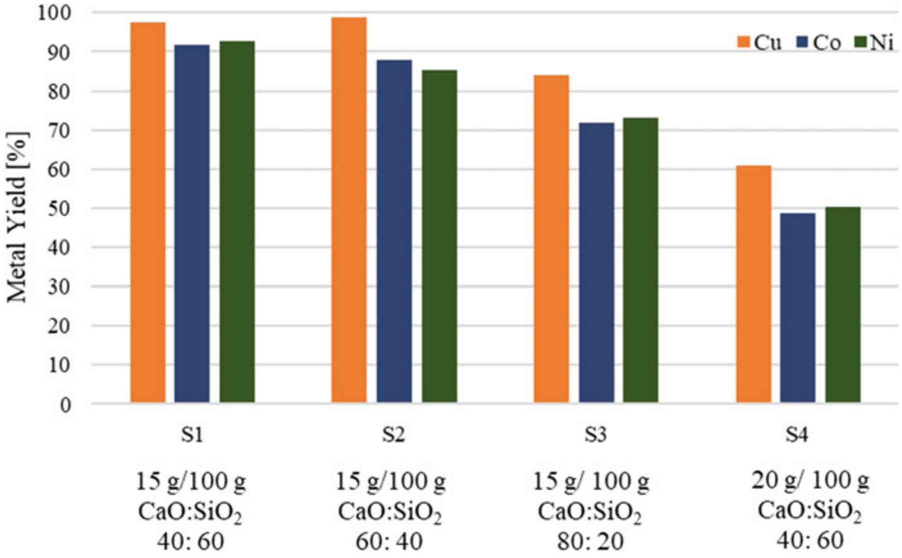


Fig. 5 Metal yields in dependence of flux composition and addition amount

The high graphite content of the input feed influences the smelting behavior and can lead to metal losses in form of non-settled metal droplets. This is reflected in the lower individual metal yields of the affected trials S3 and S4, given in Fig. 5. The presented metal yields are calculated by Eq. (4)

$$\text{Metal yield} = \frac{c_{i\ \text{in Metal}} \cdot m_{\text{Metalphase}}}{c_{i\ \text{in Li-depleted BM}} \cdot m_{\text{Li-depleted BM}}} \tag{6}$$

In case of the other two trials, high recovery-yields for the single metals are reached with up to 99% Cu, 91% Co and 93% Ni.

The slag samples were analyzed for chemical composition with except of S4, as no sufficient quantity could be obtained. Analysis results are given in Table 3.

Table 3 Elemental composition of slag samples in wt.-%

Element	Al	Ca	Si	Mn	Cu	Co	Ni	Li	F
S1	18.4	10.3	10.1	4.40	6.27	0.36	0.68	2.53	1.86
S2	19.9	13.2	6.09	7.66	0.55	0.05	0.06	2.81	2.70
S3	27.2	16.0	2.97	2.13	5.08	0.25	0.55	2.64	4.00

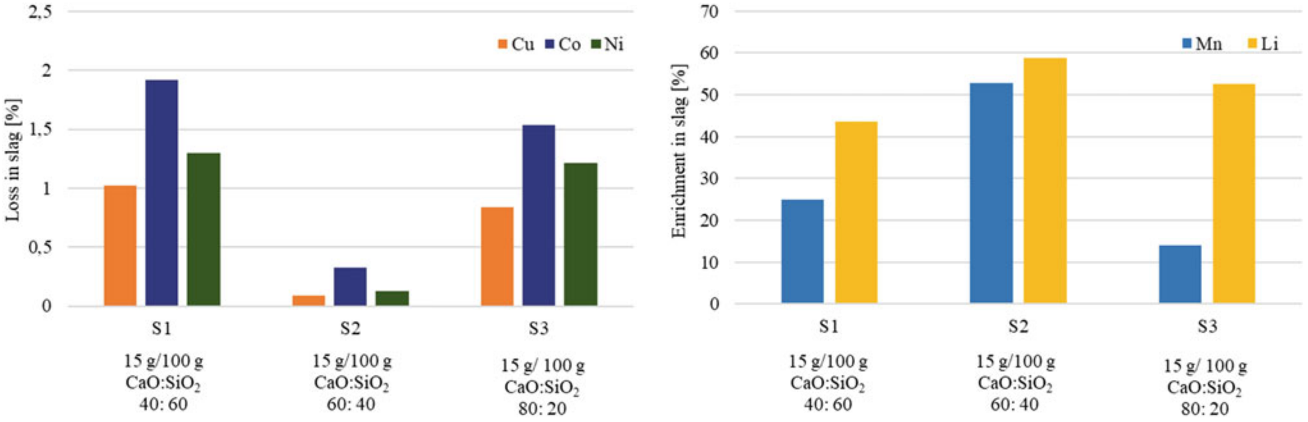


Fig. 6 Cu, Co, and Ni losses (left) and Mn and Li enrichment (right) in slag

The slags with lowest and highest CaO share (S1 and S3) have a high Cu content. But especially in case of S3, this could be due to incomplete reaction of graphite with CuO. For the addition of 15 g fluxes per 100 g black mass with the ratio of 60% CaO:40% SiO_2 (S2), the lowest Cu, Ni, and Co losses occur. This is reflected in the percentage metal loss in the slag, presented in Fig. 6.

Due to the low Cu, Co, and Ni solubility of S2, their losses in slag are each below 0.4%. Although the calculated metal yields are lower than in S1, this may be due to inhomogeneities of the input-feed, for example, a higher graphite content. This is also supported by the largest CuO addition required in S2. Calculation of Cu, Co, and Ni yields related to their quantity in slag and metal phase thus results in >99% recovery rates.

Li slagging also shows the best results for this slag system with transfer of 59% Li to the slag phase. Nevertheless, according to FactSage™ 8.0 calculations, higher Li slagging of 76% should have been possible. Li could have volatized before a liquid slag phase has formed. This would be overcome in industrial setups, when the black mass is fed into a melt phase.

S1 resulted in lower Li slagging than S2. Because of the lower CaO content in the slag, enrichment of F is hindered. This favors the volatilization of LiF and is according to thermochemical calculations. Correspondingly, the best Li slagging was predicted by FactSage™ 8.0 for the slag with the highest CaO content. But the viscosity of the slag was increased to such an extent that consumption of the graphite was hindered, and the experimental result was negatively affected. Similar trends regarding Li slagging were found in a previous study, where a whole battery shredder was melted by flux addition with the same SiO_2:CaO ratio as in this investigation [17].

3.4 Lithium Mass Flow over the Complete Process Chain

Figure 7 presents the Li mass flow over the complete process chain consisting of pyrolysis, water leaching, and smelting.

It was possible to recover 55.4% of the Li before entering the smelting process by ESLR. After the smelting operation, the known issue of Li spreading over slag and flue dust occurs. This results in the transfer of 18.5% of the initial Li input in the flue dust and 26.1% of the initial Li input in the slag phase. Therefore, the benefit of previous Li recovery is proven.

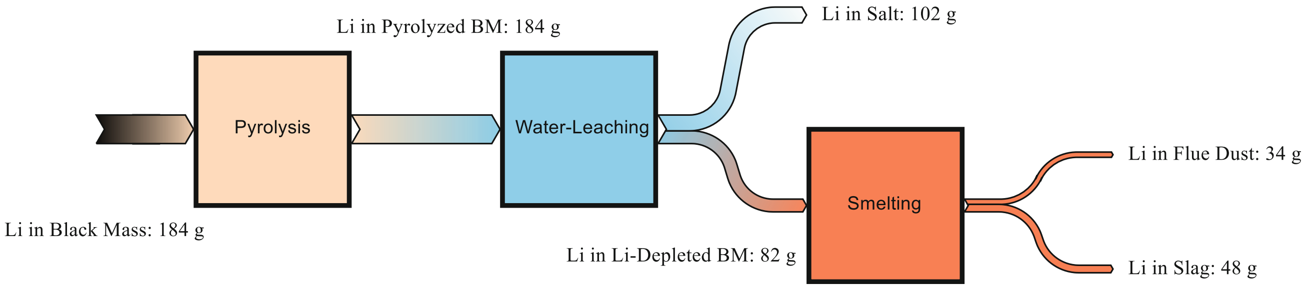


Fig. 7 Li mass flow over the process chain in case of 10 kg black mass input

4 Discussion

Achieved Ni, Co, and Cu recovery rates >99% in the presented battery recycling approach are competitive with previous studies. The biggest challenge in the melting process at this point is the sufficient use of graphite. Metal losses in the present study were mainly caused by un-settled metal droplets from the powder fraction. In a more turbulent reactor, e.g., an electric arc furnace, better graphite consumption is expected as shown in previous research [13, 14]. In this study, CuO was used as a dummy for waste streams that could be blended with battery material. If Li is recovered before the smelting operation, its dilution in the slag phase, by adding further waste streams is no longer an issue and should be investigated in the future. The concept of ESLR offers a high flexibility of process design, since slag design does not need to be optimized for recovering Li from slag or flue dust.

Regarding Li recycling, the combination of ESLR with pyrometallurgical battery recycling has been shown to be feasible and has a high potential. In the present study, a Li recovery of 55.4% is reached before entering the smelting process, and previous studies showed recovery rates of 60–70% [22, 27, 28, 33] to be possible. In thermal pre-treatment, it is important to generate process conditions as reducing as possible [28]. For this reason, the use of battery cells or non-mechanically processed and sorted battery shredder with high organic content is beneficial for higher Li recoveries. Improved delamination of collector foils and therefore maximized black mass yields in mechanical separation after a thermal treatment favor this, too. Studies on generic material blends promise further increase in Li yield beyond 70% [37–39].

Comparison of integrated ESLR with the approaches of Li enrichment in slag or flue dust points out its competitiveness. Slagging of Li differs between 72% and 82% in literature [14, 17], and it has to be taken into account that further processing such as defined cooling, crushing, possibly flotation, and an acidic leaching step are necessary to recover the Li. All of those steps could lead to Li losses and require high effort. ESLR offers an environmentally friendly alternative. Although approaches of H_2O-based Li leaching from flue dust are reported in literature [12], amount of vaporized Li is accorded to Al content of slag and total Li recovery has shown to be not higher than the reached Li recovery yields in this study by ESLR [12]. Moreover, high evaporation yields require higher temperatures of up to 1800 °C [13], and in case of high LiF shares in flue dust, acidic leaching will be required as well.

The F content of the black mass is also a challenge in recycling processes. In pyrometallurgical smelters, F leads to faster corrosion of the furnace lining and requires complex off-gas handling [5, 8]. Although 18% of fluorine could be removed by ESLR process in this study, the F content in the slag of the best trial amounts to 2.7%. Optimization of the ESLR process offers great potential to produce a usable and less corrosive slag by previous F removal in thermal treatment and water leaching.

5 Conclusion

Feasibility and the high potential of integrating ESLR into a pyrometallurgical recycling chain for LIBs were shown in this study. With improvement of Li recovery rates in the water leaching process, e.g., by choosing high organic containing input fractions for thermal treatment, an extension of the reached Li recovery rate of 55.4% to >70% is expected. This approach is an environmentally friendly, energy and chemical saving alternative for Li recovery in pyrometallurgical LIBs recycling. Metal yields of Co, Ni, and Cu are not significantly affected by ESLR, and recovery rates of >99% according to slag analysis are achieved. Main losses occur due to the high graphite content of the black mass. The most complete possible conversion of graphite with another residual stream additional to LIBs as well as the effects of blending different input feeds will be investigated in follow-up studies in addition to the optimization of the thermal treatment.

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References

1. Xu C, Dai Q, Gaines L et al (2020) Future material demand for automotive lithium-based batteries. Commun Mater:1. https://doi.org/10.1038/s43246-020-00095-x
2. IEA, International Energy Agency (2022) Global electric vehicle outlook 2022, Paris
3. BMU (2006) Richtlinie 2006/66/EG des Europäischen Parlaments und des Rates vom 6. September 2006 über Batterien und Akkumulatoren sowie Altbatterien und Altakkumulatoren und zur Aufhebung der Richtlinie 91/157/EWG
4. Proposal for a regulation of the european parliament and of the council concerning batteries and waste batteries, repealing Directive 2006/66/EC and amending regulation (EU) No 2019/1020 (2020)
5. Brückner L, Frank J, Elwert T (2020) Industrial recycling of lithium-ion batteries—a critical review of metallurgical process routes. Metals 10: 1107. https://doi.org/10.3390/met10081107
6. Pinegar H, Smith YR (2019) Recycling of end-of-life lithium ion batteries, part I: commercial processes. J Sustain Metall 5:402–416. https://doi.org/10.1007/s40831-019-00235-9
7. Pinegar H, Smith YR (2020) Recycling of end-of-life lithium-ion batteries, part II: laboratory-scale research developments in mechanical, thermal, and leaching treatments. J Sustain Metall 6:142–160. https://doi.org/10.1007/s40831-020-00265-8
8. Harper GDJ, Kendrick E, Anderson PA et al (2023) Roadmap for a sustainable circular economy in lithium-ion and future battery technologies. J Phys Energy 5:21501. https://doi.org/10.1088/2515-7655/acaa57
9. Blengini GA, El Latunussa C, Eynard U et al (2020) Study on the EU's list of critical raw materials. Final report. Publications Office of the European Union, Luxembourg
10. Georgi-Maschler T, Friedrich B, Weyhe R et al (2012) Development of a recycling process for Li-ion batteries. J Power Sources 207:173–182. https://doi.org/10.1016/j.jpowsour.2012.01.152
11. Hu X, Mousa E, Tian Y et al (2021) Recovery of Co, Ni, Mn, and Li from Li-ion batteries by smelting reduction – part I: a laboratory-scale study. J Power Sources 483:228936. https://doi.org/10.1016/j.jpowsour.2020.228936
12. Hu X, Mousa E, Ye G (2021) Recovery of Co, Ni, Mn, and Li from Li-ion batteries by smelting reduction – part II: a pilot-scale demonstration. J Power Sources 483:229089. https://doi.org/10.1016/j.jpowsour.2020.229089
13. Sommerfeld M, Hovestadt G, Friedrich B (2021) Smelting of pyrolyzed lithium-ion battery black mass using a calcium-aluminate slag system. In: EMC 2021: June 27–30, Online: European metallurgical conference: proceedings. GDMB, Clausthal-Zellerfeld, pp 879–902
14. Sommerfeld M, Vonderstein C, Dertmann C et al (2020) A combined pyro- and hydrometallurgical approach to recycle Pyrolyzed lithium-ion battery black mass part 1: production of lithium concentrates in an electric arc furnace. Metals 10:1069. https://doi.org/10.3390/met10081069
15. Windisch-Kern S, Holzer A, Ponak C et al (2021) Pyrometallurgical lithium-ion-battery recycling: approach to limiting lithium slagging with the InduRed reactor concept. PRO 9:84. https://doi.org/10.3390/pr9010084
16. Windisch-Kern S, Holzer A, Wiszniewski L et al (2021) Investigation of potential recovery rates of nickel, manganese, cobalt, and particularly lithium from NMC-type cathode materials (LiNixMnyCozO2) by carbo-thermal reduction in an inductively heated carbon bed reactor. Metals 11:1844. https://doi.org/10.3390/met11111844
17. Stallmeister C, Scheller M, Friedrich B (2023) Slag design for pyrometallurgical metal recycling and targeted lithium slagging from lithium-ion batteries. In: Proceedings of 8th International Slag Valorization Symposium
18. Competence Cluster Recycling & Green Battery GreenBatt-Projects. https://www.greenbatt-cluster.de/en/projects/pyrolith/
19. Holzer A, Wiszniewski L, Windisch-Kern S et al (2022) Optimization of a pyrometallurgical process to efficiently recover valuable metals from commercially used lithium-ion battery cathode materials LCO, NCA, NMC622, and LFP. Metals 12:1642. https://doi.org/10.3390/met12101642
20. Dang H, Wang B, Chang Z et al (2018) Recycled lithium from simulated pyrometallurgical slag by chlorination roasting. ACS Sustain Chem Eng 6:13160–13167. https://doi.org/10.1021/acssuschemeng.8b02713
21. Klimko J, Oráč D, Miškufová A et al (2020) A combined pyro- and hydrometallurgical approach to recycle pyrolyzed lithium-ion battery black mass part 2: lithium recovery from Li enriched slag—thermodynamic study, kinetic study, and dry digestion. Metals 10:1558. https://doi.org/10.3390/met10111558
22. To be published, Stallmeister C, Friedrich B (2023) Holistic investigation of inert thermal treatment of industrially shredded NMC 622 lithium-ion batteries and its influence on selective lithium recovery by water-leaching. Metals
23. Stallmeister C, Schwich L, Friedrich B (2020) Early-Stage Li-Removal – Vermeidung von Lithiumverlusten im Zuge der Thermischen und Chemischen Recyclingrouten von Batterien. In: Holm O, Thomé-Kozmiensky E, Goldmann D et al (eds) Recycling und Rohstoffe. Thomé-Kozmiensky Verlag GmbH, Neuruppin, pp 544–557
24. Schwich L, Schubert T, Friedrich B (2021) Early-stage recovery of lithium from tailored thermal conditioned black mass part I: mobilizing lithium via supercritical CO_2-carbonation. Metals 11:177. https://doi.org/10.3390/met11020177
25. Sabarny P, Peters L, Sommerfeld M et al (2020) Early-stage lithium recovery (ESLR) for enhancing efficiency in battery recycling. Unpublished, Wiesbaden
26. Vanderbruggen A, Gugala E, Blannin R et al (2021) Automated mineralogy as a novel approach for the compositional and textural characterization of spent lithium-ion batteries. Miner Eng 169:106924. https://doi.org/10.1016/j.mineng.2021.106924

27. Balachandran S, Forsberg K, Lemaître T et al (2021) Comparative study for selective lithium recovery via chemical transformations during incineration and dynamic pyrolysis of EV Li-ion batteries. Metals 11:1240. https://doi.org/10.3390/met11081240
28. Rouquette LMJ, Lemaître T, Vieceli N et al (2023) Intensification of lithium carbonation in the thermal treatment of spent EV Li-ion batteries via waste utilization and selective recovery by water leaching. Resour Conserv Recycl Adv 17:200125. https://doi.org/10.1016/j.rcradv.2022.200125
29. Lombardo G, Ebin B, St. J. Foreman MR et al (2019) Chemical transformations in Li-ion battery electrode materials by carbothermic reduction. ACS Sustain Chem Eng 7:13668–13679. https://doi.org/10.1021/acssuschemeng.8b06540
30. Lombardo G, Ebin B, Steenari B-M et al (2021) Comparison of the effects of incineration, vacuum pyrolysis and dynamic pyrolysis on the composition of NMC-lithium battery cathode-material production scraps and separation of the current collector. Resour Conserv Recycl 164: 105142. https://doi.org/10.1016/j.resconrec.2020.105142
31. Haynes WM (2017) CRC handbook of chemistry and physics: a ready-reference book of chemical and physical data, 97th edn. CRC Press, Boca Raton, London, New York
32. Li J, Wang G, Xu Z (2016) Environmentally-friendly oxygen-free roasting/wet magnetic separation technology for in situ recycling cobalt, lithium carbonate and graphite from spent LiCoO2/graphite lithium batteries. J Hazard Mater 302:97–104. https://doi.org/10.1016/j.jhazmat.2015.09.050
33. Schwich L, Friedrich B (2022) Environmentally friendly recovery of lithium from lithium–sulfur batteries. Metals 12:1108. https://doi.org/10.3390/met12071108
34. Park S, Jung S, Kwon D et al (2022) Carbothermic reduction of spent lithium-ion batteries using CO_2 as reaction medium. Chem Eng J 435: 135165. https://doi.org/10.1016/j.cej.2022.135165
35. Bale CW, Bélisle E, Chartrand P, Decterov SA, Eriksson G, Gheribi AE, Hack K, Jung IH, Kang YB, Melançon J, Pelton AD, Petersen S, Robelin C, Sangster J, Spencer P, Van Ende MA (2010–2016) FactSage thermochemical software and databases. Elsevier
36. Li J, Huang S (2020) Recycling of lithium slag as a green admixture for white reactive powder concrete. J Mater Cycles Waste Manag 22:1818–1827. https://doi.org/10.1007/s10163-020-01069-4
37. Liu P, Xiao L, Tang Y et al (2019) Study on the reduction roasting of spent LiNixCoyMnzO2 lithium-ion battery cathode materials. J Therm Anal Calorim 136:1323–1332. https://doi.org/10.1007/s10973-018-7732-7
38. Hu J, Zhang J, Li H et al (2017) A promising approach for the recovery of high value-added metals from spent lithium-ion batteries. J Power Sources 351:192–199. https://doi.org/10.1016/j.jpowsour.2017.03.093
39. Xiao J, Li J, Xu Z (2017) Recycling metals from lithium ion battery by mechanical separation and vacuum metallurgy. J Hazard Mater 338:124–131. https://doi.org/10.1016/j.jhazmat.2017.05.024