



Observations on the Leaching of Milled Black Mass with Additives

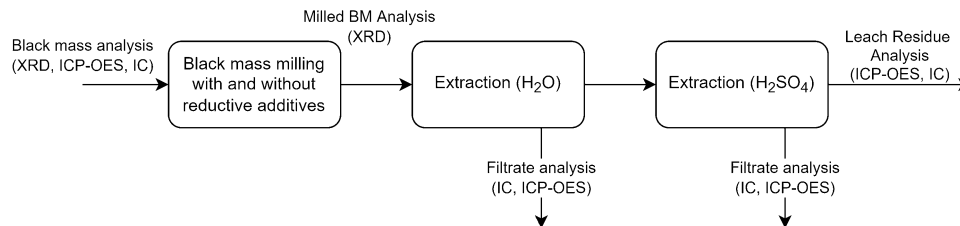
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Abstract

In this work, previously produced black mass was treated in sequence by milling, water leaching, and sulfuric acid leaching. Two goals were set: first, whether milling, with reductive additives, could impart reductive phase changes which would allow Li extraction to water in the water leaching; second, co-leaching of the black mass with the additive, CoS, was explored as to ascertain whether synergistic effects could be detected in a leaching system composed of reductive (CoS) and oxidative (NMC oxides) materials in the presence of redox mediator ($\text{Fe}^{2+}/\text{Fe}^{3+}$ redox pair). It was found out that in all experiments, similar Li concentration was obtained despite milling. Fluoride analysis indicated high F concentrations in the water solution and implicated formation of insoluble products such as LiF(s) . Water-soluble fluoride ended up in all fractions: water leaching filtrates (ca. 500 mg/L), acid leaching filtrates (ca. 800–1700 mg/L), and leach residues (ca. 68–382 mg/kg). In acidic leaching, CoS appeared to enhance extraction of elements from cathode-active materials, improving extraction from 78 to 92% for Ni under relatively mild leaching conditions ($T=30\text{ }^{\circ}\text{C}$, solid conc. = 100 g/L, $[\text{H}_2\text{SO}_4]=1.4\text{ M}$).

Graphical Abstract



Keywords Recycling · Hydrometallurgy · Li-ion batteries · Milling · Fluoride

Introduction

Lithium-ion batteries that are expended and recycled usually result in material streams that include electrode foils (Al and Cu), casings, and wirings and a fine fraction, entitled black mass (BM). This BM is composed of, as a result of physical separation operations, fine materials present in batteries. These include cathode and anode active materials, usually lithiated mixed NiMnCo oxides and graphite,

respectively. The oxide materials are of interest to industry and society as they contain large quantities Li, Ni, Co, and Mn in a concentrated form. There are several strategies that are being investigated for the recycling of these materials, including regenerative (direct re-use after conditioning), re-manufacturing (breaking of chemical bonds, but going back to cathode materials), and total downcycling of the elements into new raw materials of, e.g., battery grade. Total downcycling strategy can rely on variety of different processing options. These include fundamentally different strategies, starting from pyrometallurgical treatment to mechanical pre-treatment and, in both cases, to hydrometallurgy. In the field of hydrometallurgy, there exists a plethora of different studies involving different acid leaching systems for treating spent Li-ion batteries [1–3]. Similarly, researchers have

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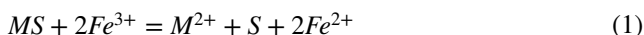
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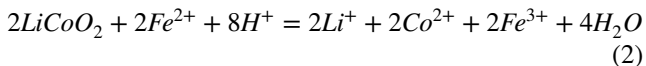
designed several possible pre-treatment pathways for spent batteries.

First, in the present study, the impact of milling on the extractability of elements from black mass was investigated. It was hypothesized that by utilizing reductive reagents in the milling, one could potentially cause changes to crystal structure that would allow better extraction of Li into a water phase after milling but before acidic leaching. Previous studies have shown that mechanochemical treatment can result in reduction of the high-valence oxides, to the point that the resulting phases contained metallic Co [4–6]. Furthermore, it is known from previous studies that the Al cathode foils tend to not completely separate from the powder that is attached to the foils with polyvinylidene fluoride (PVDF) binder. It was hypothesized that the milling would induce crystal structure changes, either via physically induced changes (deformation, faults, and cracks) or via physico-chemical change (phase changes, phase change-induced deformation) and that this, in turn, could either hamper or improve Li extraction in H₂O leaching.

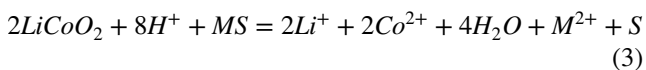
Secondly, after milling, the impact of a metal sulfide on extractability of Ni, Co and Mn in acid leaching was investigated. The same additives that were present in milling and water leaching were subsequently subjected to acidic leaching. To the best of the authors' knowledge, this is the first time leaching of black mass is attempted with sulfidic raw materials and the results could be generalized to either a primary process utilizing black mass as a part of the feed or a recycling process utilizing primary raw materials, such as NiCoS, as a leaching additive. CoS is a material with reductive properties. It is commonly known in hydrometallurgy that metal sulfides are extractable to varying degrees via oxidation of sulfidic S by ferric Fe [7–9], Eq. (1):



It is also known that the cathode materials present in BM can undergo similar reaction which is reductive instead of being oxidative, Eq. (2) [10–12]:



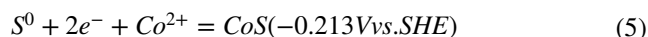
In the present study, it is suggested that the leaching can occur in a catalytic manner according to Eq. (3):



The primary interest of the study was to learn whether a common MS (M=Co or Ni) intermediate product could enable leaching of the black mass without external reductant. Ni²⁺ and Co²⁺ in the S²⁻ would be part of the product, i.e., the reductant would ideally be a reagent expenditure, but raw materials to the process. S²⁻ would bring the actual reductive power to the system, as shown in Eq. (4).



However, it is unlikely that S²⁻ would remain stable in the lixiviant and be the reductant acting upon the cathode materials. Direct reduction of the compound is possible via ferrous–ferric-mediated redox catalysis, leading to lower available reduction potential as shown in Eq. (5):



Creation of elemental S can potentially hinder the dissolution of the MS concentrate. The MS compounds are usually quite stable, and it is possible that their reductive properties can't be efficiently utilized. However, to the best of the author's knowledge, no information is available on how such materials behave when oxidized in a system with cathode-active material oxides. In this study, the water-soluble F⁻ content of the material was also examined by means of ion-exchange chromatography in each of the hydrometallurgical experiments.

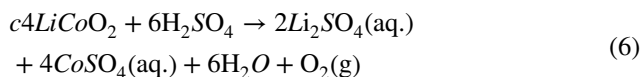
Experimental

Raw Material and Chemicals

Spent black mass were utilized in this work. The black mass was obtained from previous study where spent lithium-ion batteries from e-bikes were mechanically processed by primary crushing, sieving, magnetic, and eddy current separation [13]. Particle size analysis of the black mass with 1000 μm, 500 μm, and 125 μm sieve stack (Retsch AS300 Control) indicated that D90 and D50, presenting the cut point under which 90% or 50% of particles exist, in the sample was 861 and 350 μm, respectively. The black mass was semi-quantitatively characterized by powder x-ray diffraction (XRD, PANalytical X'Pert3 Diffractometer, Cu Ka, 40 kV, 40 mA, 0.013 step, and scan rate of 0.2/s) for crystalline phases as well as amorphous phases by standard addition method. Digestion was conducted with HF, HNO₃, HCl, and HClO₄ after which the undissolved residue was filtered off, the solution was evaporated off and the residue redissolved in HNO₃ prior to the analysis, and inductively coupled plasma optical emission spectroscopy (ICP-OES) was utilized in compositional analysis of BM. Li was determined with Perkin Elmer 7300DV and the other elements with Thermo Scientific 6500 Radial. The water-soluble F present in the material was analyzed by treating 0.5 g sample with 25 g of H₂O, which was subsequently subjected to ion-chromatography (IC, Metrohm 850 Professional, a Metrosep Anion column). The results of semi-quantitative phase (XRD) and quantitative element composition

(ICP-OES) characterization are shown in Table 1. Different cathode-active materials were identified, including $\text{Li}_2\text{Mn}_2\text{O}_4$ (LMO), LiCoO_2 (LCO), LiFePO_4 (LFP), and $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ (NMC-111).

In this work, H_2SO_4 (97% Analar NORMAPUR, VWR BDH Chemicals) was utilized in leaching. Diluted H_2SO_4 solutions (1.4 M) were prepared by dilution with de-ionized water. The leaching reaction for the cathode materials in H_2SO_4 was suggested by Nan et al. [14] such as in Eq. (6):



Each mol of Co requires 1.5 mol of H_2SO_4 . Similar estimates can be assumed to hold with the NMC and LMO type oxides that were contained in the black mass in this study as shown by XRD in Table 3. The synergistic leaching equation indicated that 2 mol of H_2SO_4 per mol Co would be required.

Experiments

Experiments were designed to study phenomena in two singular unit processes: water leaching of the milled BM, followed by acidic leaching of the milled and H_2O -leached BM. The experimental parameters were modified progressively from the baseline (Exp. 1: acidic leaching without H_2O & Exp. 2: H_2O and acidic leaching) by including milling (Exp. 3–5) and additives (Exp. 4–5). The experimental matrix is shown in Table 2. It is important to mention that the aluminum foils were used directly from the crushing process, without any additional purification.

The experimental series 3–5 begun with milling of the material with a vibrating ring mill (Siebtechnik 250). Milling was performed in intervals of 60 s for a total of 20 min. The chamber lid of the mill was opened between the intervals to release any potential gases. During this procedure, the temperature was measured between the milling intervals with an infrared camera (thermoIMAGER TIM 40). A HF alarm was placed next to the mill chamber to monitor any potential $\text{HF}(\text{g})$ release. As an additive, in some

Table 1 The black mass sample composition reported by elemental composition (ICP-OES) and semiquantitative phasic analysis (XRD)

Phase (XRD)	C 3R	C 2H	NMC-111	LMO	LCO	LFP	Cu(s)	CuO	A
wt.%	12.8	38.9	6.0	3.1	0.9	4.8	TR	1.6	31.9
Element (ICP-OES)	Al	Co	Cu	Fe	Mn	Ni	F	Li	
wt%	1.3	3.6	3.2	3.0	5.9	3.4	0.8	2.5	

A amorphous

Table 2 The reagents and raw materials utilized in each experiment

Exp	1	2	3	4	5
Milling	No	No	Yes	Yes	Yes
Leaching	Acidic	H_2O + acidic	H_2O + acidic	H_2O + acidic	H_2O + acidic
BM (g)	14.56	15.05	15.02	15.05	14.97
CoS (g)	x	x	x	2.69	2.7
Mass of Al Foils (g)	x	x	x	x	8.01
Count of Al Foils (pieces)	x	x	x	x	41

Exp. 1 and 2 acted as baseline experiments for water leaching and acid leaching. Exp. 3 added milling. Exp. 4 and 5 added different additives. Water leaching was performed at $T=30\text{ }^\circ\text{C}$, $t=60\text{ min}$ and solid conc. = 100 g/L. Acid leaching was done with $[\text{H}_2\text{SO}_4]=1.4\text{ M}$, $t=120\text{ min}$, $T=30\text{ }^\circ\text{C}$

Table 3 The semi-quantitative XRD results (%) of the phase content of the milled materials (Exp. 3–5)

Sample	C 3R	C 2H	NMC-111	LMO	LCO	LFP	Cobalt-pentlandite (CoS)	Cobalt sulfide ($\text{Co}_{1.82}\text{S}_{2.08}$)	Cu	CuO	A
Exp. 3	15.8	16.9	11.8	6.9	1.9	11.1	0.0	0.0	0.9	0.8	33.9
Exp. 4	12.1	12.0	8.4	4.8	1.4	9.2	3.4	1.6	0.8	0.6	45.7
Exp. 5	20.1	1.7	13.2	7.6	0.9	10.9	2.3	1.1	1.6	0.7	39.9

experiments, synthetic CoS (99.5%, Thermo Fisher Scientific) and Al foils from previous mechanical processing [13] were utilized. After sieving, the -1000 μm fractions were combined, characterized with XRD and transferred to H_2O leaching.

In H_2O leaching, de-ionized H_2O was utilized. Initial solid conc. was 100 g/L and leaching was performed for $t=60$ min at $T=30$ °C. After H_2O leaching, the materials were vacuum filtrated and washed. The filtrate was analyzed with IC for fluoride (F) and for Al, Cu, Fe, Co, Ni, Li, and Mn with ICP-OES. The water-leached leach residues were then subjected to the acid leaching which was performed in a 250 mL beaker. The oxidation–reduction potential (ORP), or redox potential of the solution, was measured with combination ORP electrode O14/DJ/PC/NS/SR/TEF/PTBND/12 \times 300 M/BNC (Sentek, UK) connected to Consort 3210, Consort bvba (Belgium). Heat plate with magnetic stirring was utilized, and the temperature of the plate was maintained at $T=30$ °C, $[\text{H}_2\text{SO}_4]=1.4$ M, $t=120$ min, and with initial solid conc. of 100 g/L. *Ca.* 15 g of BM was utilized per experiment. The quantity of acid utilized in experiments was in stoichiometric excess.

Temperature increase during leaching experiments was recorded. The filtration procedure was identical to what was done after water leaching. The leach residue masses were recorded, both wet and dried. The leach residues were acid digested (four acid digestion) and resulting solutions were analyzed with ICP-OES to obtain leach residue mass fractions. During the experiments, $\text{HF}(\text{g})$ emissions were assumed to occur and personal protective equipment was utilized.

Results and Discussion

Black Mass Milling and Characterization

The milled materials were characterized with XRD prior to leaching. The baseline black mass in this study contained different cathode oxides, LiFePO_4 , as well as allotropies of graphite, as is shown previously in its characterization (Table 1). Characterization of milled samples (identified phases and semi-quantitative quantification) is shown in Table 3. It is possible that a phase change occurred in the CoS due to milling as the presence of two different Co phases was identified, with the other having S in lower oxidation state. The diffractograms and the fitting are shown in Supplementary Materials A1.

Sieving analysis of milled samples revealed that the share of particles with particle size above 125 μm was 23.2 wt%, 25.4 wt%, and 22.5 wt% for Exp. 3, Exp. 4, and Exp 5., respectively, a decrease from the original (78.6 wt.%). Particles above 125 μm may be composed of single particles

which were not pulverized or alternatively of aggregates which were generated during the comminution. However, this distinction remains unclear as no further verification was conducted. In regard to additives affecting the comminution, no significant difference between experiments was detected.

The temperature profiles obtained between the milling intervals during the milling experiments showed an increase of 23 to 25 °C, finishing at temperatures of 46 °C for both Exp. 3 and 4 and at 49 °C for Exp. 5. This moderate increase was not enough to generate $\text{HF}(\text{g})$ in a detectable manner. When the XRD and sieving analysis are taken together, it can be concluded that 20 min comminution performed in this study was not enough to produce the energy required for deformation of crystals. As the relative quantity of amorphous material did not significantly increase, the milling could be concluded to have been unsuccessful. Assumably, particles were pulverized and partially also aggregated but did not reach the stage where considerable accumulation of defects, amorphization, formation of meta stabile polymorphous forms, and chemical reactions occur [15]. Therefore, it was expected that no marked improvement in Li extraction would be seen in subsequent water leaching. However, this did not prevent the further investigation of the leaching behavior of the combined materials, with and without milling, and the study was continued.

Water Leaching

Water leaching was done for all experiments apart from Exp. 1. The impact of milling of the black mass with reductive materials on the Li extraction to H_2O medium was investigated. The extraction to solution, in general, was calculated as follows:

$$\% = \frac{c_{\text{H}_2\text{O}} \cdot m_{\text{H}_2\text{O}}}{c_{\text{LR}} \cdot m_{\text{LR}} + c_{\text{H}_2\text{O}} \cdot m_{\text{H}_2\text{O}} + c_{\text{H}_2\text{SO}_4} \cdot m_{\text{H}_2\text{SO}_4}} \quad (7)$$

where $c_{\text{H}_2\text{O}}$ is the concentration of an element in the water, $m_{\text{H}_2\text{O}}$ is the mass of the filtrate, c_{LR} is the mass fraction of an element in the leach residue, and m_{LR} is the mass of the dry leach residue and $c_{\text{H}_2\text{SO}_4}$ which is the concentration of an element in the acidic leachate after filtration and $m_{\text{H}_2\text{SO}_4}$ is the mass of the filtrate. The concentrations are summarized in Supplementary Materials A2. The extraction results are presented in Table 4. It is worth noting that a significant fraction of water-soluble or labile F compounds and Li ends up into the H_2O solution: at best, extraction of F was 42.7% and Li 29.9%. This result, however, clearly indicates that water washing is insufficient in removing all F sourced from LiPF_6 , Exp. 2 and Exp 3. were the experiments with no milling and milling without additives, respectively. The quantity of F present in the material is dependent on its pre-treatment

Table 4 The water leaching results, reported as extraction % from the black mass to solution

Exp	% Al	% Co	% Cu	% Fe	% Mn	% Ni	% F	% Li
2	0.84	0.18	0.29	0.16	0.25	0.13	42.7	29.9
3	0.28	0.02	0.02	0.01	0.24	0.01	31.6	21.5
4	0.30	0.01	0.03	0.02	0.27	0.02	34.7	24.1
5	0.26	0.01	0.00	0.00	0.05	0.00	40.1	18.4

Exp. 2=no milling, no additives; Exp. 3=milling, no additives; Exp. 4=milling, CoS additives; Exp. 5=milling, CoS and Al foil additives

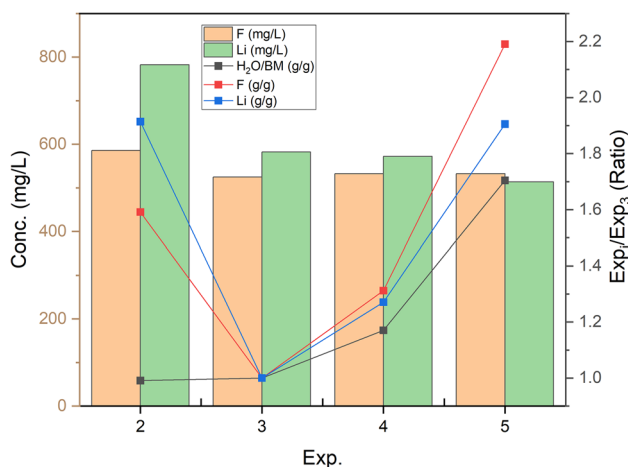


Fig. 1 Dissolved F and Li during water leaching (left Y-axis) and the relative quantity of H₂O per BM, where Exp. 3 acts as a baseline for comparisons between dissolved Li, F, and water to black mass ratio. Milling was done for Exp. 3–5, no milling was done for Exp. 2. H₂O to BM is the ratio of the masses of black mass per water utilized in an experiment

history as LiPF₆ is known to be labile and react with both moisture and heat to release HF(g).

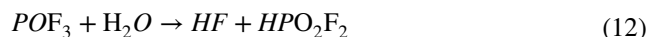
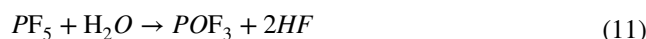
Subsequently, seeing that only F and Li were appreciably extracted during the water leaching, the concentrations of the resulting water leachates were examined and related to the solution volumes. The amount of water added in each experiment was done according to Eq.:

$$m_{H_2O} = 10 \cdot (m_{BM} + m_{additives}) \quad (8)$$

where m_{BM} is the mass of black mass sample and $m_{additives}$ is the mass of any additives. It was observed that despite varying the ratio of mass of water and black mass, concentrations remained similar between the experiments, Fig. 1. These comparisons were calculated as follows:

$$Exp_i/Exp_3 = \frac{m_i}{m_3} \quad (9)$$

where m_i is the mass of the element (Li or F) in Exp. no. i ($i=2-5$) and m_3 is the mass of the Li or F in Exp 3., respectively. The H₂O to BM is the ratio of mass of water per mass of black mass. This equivalence in Li and F concentrations between experiment most likely indicates the formation of insoluble compounds at solubility limit. One such candidate for an insoluble compound is LiF(s) whose solubility in H₂O ranges between 1.34 g/L and 1.5 g/L in the temperature range of 25 to 80 °C [16]. LiF exists in equilibrium with LiPF₆ in water, alongside with PF₅ [17]. LiPF₆ is also thermally sensitive, generating LiF(s) and PF₅(g) at relatively low temperatures of > 80 °C [18, 19]. PF₅ is reactive toward moisture and has been suggested to hydrolyze in sequence [17, 20, 21]. It has been suggested in prior literature that LiPF₆ reaction path is as follows, possibly hydrolyzing all the way to HF, LiF, and H₃PO₄ [17, 18, 20, 21]:



These compounds intrinsically bind together the issue of fluoride management and comprehensive Li recovery in any recycling process utilizing unit processes that contain water.

Exp. 2 had concentration of 700 mg/L of Li, the rest (Exp. 3–5) had 500 mg/L. Coincidentally, this may be an effect of milling (Exp. 2 vs. Exp. 3–5). Based on solubility limit of 1.37 g/L for LiF at 30 °C, the solubility limit for Li in the presence of F could be calculated to be at a level of 367 mg/L. Hence, it is likely that the solution in the present study is already saturated in terms of LiF(aq.) and no more either Li or F could be extracted into the aqueous phase, which is a hypothesis that can be examined. However, this estimate is complicated by the possible presence of fluoride complexes from the hydrolysis of PF₅ and its reaction products. Future studies should target this issue as it is poorly understood in which form F is present in the recycling processes, although data exist of more controlled conditions exist [20, 21]. Since the solid concentration was kept the same between the experiments

according to Eq. (8), the relative quantity of black mass to added water changed between the experiments Exp. 2 and 3 vs. 4 and 5. This allows the examination of quantity of dissolved Li and F as a function of black mass vs. added water quantity. Although the Li and F concentrations do not change between the milled samples (Exp. 3–5), there is an increase in dissolved Li (54, 68 and 101 mg in Exp. 3–5, respectively) and F (48, 63, and 104 mg in Exp. 3–5, respectively) quantity.

Based on the IC analyses, in all H₂O leaching experiments, there was a stoichiometric molar excess of F/Li ranging from the lowest in Exp. 2: 3.4 (mol/mol) to highest in Exp. 5: 5.0 (mol/mol). In Exp 3 and 4, the F/Li molar ratio was 4.8 and 4.3 (mol/mol), respectively. The results indicate that LiPF₆ was present in the black mass at the time of water leaching. The excess F/Li molar ratios could be expected to worsen the solubility of LiF. The pH of the water leaching solutions ranged between 8.9 and 9.2, which could help explain why Li solubility was higher than what was reported in the literature for water. Boiling was detected during the vacuum filtration of water leaching slurries. This likely was a result of evaporation of organic electrolytes (organic carbonates) as the pH was high enough for F to exist as a free anion. Vacuum distillation is utilized by some recycling companies in the removal of the electrolytes from crushed black mass [22]. It was also noted that the water leaching filtrate of Exp. 2 (un-milled) was brownish, whereas Exp. 3–5 (milled) were clear, potentially indicating that the temperature increase caused by milling may have resulted in chemical changes in the material.

The results of the present study suggested that the water leaching of the material will result in a challenging splitting of significant portion of Li into aqueous solution while retaining over 60% of Li in the black mass. The presence of F prevented the study of the original hypothesis of enabling Li extraction by water after a reductive milling stage. Subsequently, the new solution stream would be dilute, limiting the viable pathways for industrial processes that aim at minimizing Li losses.

Acidic Leaching

The acid leaching was performed after the water leaching (Exp. 2–5) or as the sole leaching step (Exp. 1). The main feature of the acidic leaching of this study was the investigation on the influence of the additives, mainly cobalt sulfide (synthetic cobalt pentlandite) and Al foils, on the leaching efficacy of elements in H₂SO₄ leaching with milling pretreatment (Exp. 3–5). The acid leaching results are presented in Table 5. The mass balance-based extraction percentage was calculated with Eq. (13):

$$\% = \frac{c_{H_2SO_4} \cdot m_{H_2SO_4}}{c_{LR} \cdot m_{LR} + c_{H_2O} \cdot m_{H_2O} + c_{H_2SO_4} \cdot m_{H_2SO_4}} \quad (13)$$

where the c_{H_2O} is the concentration of an element in the water, m_{H_2O} is the mass of the filtrate, c_{LR} is the mass fraction of an element in the leach residue, and m_{LR} is the mass of the dry leach residue and $c_{H_2SO_4}$ which is the concentration of an element in the acidic leachate after filtration and $m_{H_2SO_4}$ is the mass of the filtrate. The leach residue composition analyses are shown in Supplementary Materials A2. It was shown that most of the water-soluble fluoride (i.e., not PVDF) is removed under acidic treatment (Exp. 1). Additional F was dissolved in acidic leaching after water leaching in all Exp. 2–5. This result further suggests that it is probable that during the water leaching, insoluble salts of F (e.g., LiF) are formed, but whose chemical bonds are thence broken in the acidic leaching solution. In all acidic leaching experiments, the measured pH after leaching was < 0.5, i.e., there was sufficient acid in all the experiments. F concentrations in acidic leaching ranged between 800 and 1700 mg/L per experiment. As glass laboratory ware was utilized in the experiments, it is also possible that some of the HF has reacted with SiO₂. Notably, extraction was high for Co, Ni, and Mn even though the leaching was conducted with relatively high solid concentration (100 g/L) at low temperature (ca. 30 °C) with literature-comparable concentration of H₂SO₄ [10, 23, 24]. It is hypothesized that the reason for the high extraction without an external reductant (Exp. 1) was caused by several factors. First, several researchers have shown that Cu [25–27], Al and Fe [10, 11] all can enhance

Table 5 The acidic leaching results, reported as extraction % from the black mass to acidic solution

Exp	% Al	% Co	% Cu	% Fe	% Mn	% Ni	% F	% Li
1	90 (90)	91 (91)	99 (99)	81 (81)	82 (82)	88 (88)	99 (99)	97 (97)
2	77 (78)	83 (83)	99 (99)	81 (81)	72 (72)	81 (81)	58 (100)	66 (95)
3	98 (98)	85 (85)	99 (99)	77 (77)	93 (93)	78 (78)	68 (99)	76 (97)
4	96 (96)	33 (33)	98 (98)	84 (84)	96 (97)	92 (92)	65 (98)	74 (98)
5	95 (95)	36 (36)	50 (50)	90 (90)	97 (97)	96 (96)	56 (99)	79 (99)

Numerical values within brackets are the sum of the extraction to water and extraction to acid. The additives are considered in the extraction calculations

extraction significantly in the role of a reductant. Furthermore, it has been recently shown by other researchers that LFP can fill similar role as a reductant [28], probably either due to the dissociation of the ferrous Fe from the LiFePO_4 or due to the extraction of Li from LFP crystal structure which necessitates transfer of electrons from the LiFePO_4 when Li is extracted in order, for the solid material, to maintain electron balance. The presence of LFP was unfortunate as it most likely somewhat confounded the beneficial effect of the sulfidic addition as indicated by the results of prior researchers [28]. Improvements in the extractions for Ni and Mn were detected in the experiments where the sulfidic additives were utilized: Ni extraction increased from 78 wt.% in Exp. 3 to 92 wt.% and 96 wt.% in Exp. 4 and Exp. 5, respectively. Ni and Mn can be considered as a good indicator on the cathode material dissolution as the cathodes are their only source, and both are present in all the cathode oxides except for LCO and LFP. Although it appears that the additives such as CoS with milling can help in achieving a higher extraction, more maximal extraction should be attained. It needs to be noted as well that in this study it was not investigated separately how CoS impacts leaching without milling. Furthermore, the subsequent process stages would need to be designed to accommodate the separation of graphite from the undissolved sulfides: only 33–36% of the Co dissolved in the experiments where CoS was utilized as an additive.

Although solid concentration was kept at 100 g/L between experiments, the relative quantity of acid solution to black mass was higher when additives was mixed with the black mass sample. Meshram et al. have shown that this can impact extraction by *ca.* 5% under the conditions of their experiments when going from solid concentration of 100 g/L to 50 g/L [23]. In Exp. 4, the BM content decreased from 100 to 85% (Table 2), i.e., from 100 g/L to 85 g/L of BM. Hence, the change on BM solid concentration is unlikely to be the sole reason for improved extractions. This is a promising result for utilizing an industrially available intermediates as a reductant in the black mass leaching, and the subsequent challenge is whether there exists a method for treating the resulting leach residue. This was not, however, the main objective of the study, but whether the additives enhance extraction of the key elements. Previous studies have indicated that systems with Fe as an reducing catalyst may work even better under low acid concentration [11, 12].

During the acid leaching, the oxidation–reduction potential (ORP), or redox, of the solution of all experiments was measured, Fig. 2. ORP measurement yields information about the equilibrium redox reactions that are occurring in the solution. Exp. 5, which contained both CoS and Al as additives, gave the lowest ORP: *ca.* 70 mV vs. Ag/AgCl. This was most likely due to Al addition as in Exp. 4, which had only CoS, produced a higher redox potential of the solution. The sub-100 mV (vs. Ag/AgCl) redox potential can

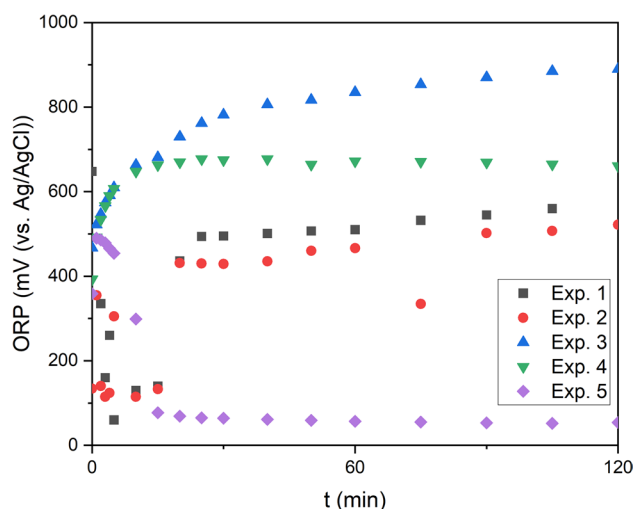


Fig. 2 ORP (mV vs. Ag/AgCl) as a function of time in all acidic leaching experiments. The data point at $t=75$ min is an erroneous reading

be taken as indication of all the oxidative materials having been reacted out and that only an excess of reductive raw materials remained. As this only occurred in Exp. 5, it likely indicates that the CoS was not as efficient reductant as Al under these conditions and ferric ions were not efficiently reduced to ferrous ions. For instance, it has been shown recently by Chernyaev et al. that Al is capable of reducing cathode-active materials [27]. Furthermore, Chernyaev et al. have shown that metallic Cu can be cemented on Al foils. In the present study, Cu extraction was anomalously low in Exp. 5 only: 50% (vs. >90% in the rest of the experiments). The poor Cu extraction in Exp. 5 supports the hypothesis that reduction was efficient to the point that the solution was not capable of redissolving cemented Cu.

Leach Residues

The leach residues were analyzed after acidic leaching experiments for elemental contents. In particular, the S content of the LR in Exp. 4–5 was analyzed. There are two possible pathways for S to escape the solid leach residues in the investigated system: due to acid attack, as $\text{H}_2\text{S}(\text{g})$, and, due to oxidative dissolution, as SO_4^{2-} anion. Based on stoichiometric calculations of the additions, 706 and 784 mg of S were added into Exp 4 and 5, respectively, while 518 and 707 mg of S were found to be present. Some decrease was measured in the experiment with CoS as only additive (Exp. 4). In case of F, IC analyses of digested leach residues indicated that the residues contained 68–382 mg/kg of water-soluble fluoride, despite the water leaching, acidic leaching, and washing of leach residue. The masses of dry leach residues were recorded as well. In general, it would

appear that milling did not have any appreciable effect on the dissolution of the additive-free samples, and neither did the H₂O leaching as a pre-treatment as in Exp. 1–3 all the undissolved mass fraction is 40–43 wt%. Leach residue analyses indicated that the Al content in Exp. 5 was not drastically different from other experiments (30 mg Al vs. 3–50 mg Al in Exp. 5 vs. Exp 1–4 leach residue, respectively), indicating that the added foils most likely dissolved near-completely. Undissolved fractions for exp. 3, 4 and 5 were 42%, 48%, and 43%.

Finally, the reliability of the fluorine analysis was evaluated via mass balance inspection. The expected quantities of F present in the black mass samples were calculated based on the black mass composition analysis (Table 1). Similarly, the composition was re-created based on the characterization of the composition of water leaching filtrate, acid leaching filtrate, and leach residue (Supplementary Materials A2). These two results were then compared. Hence, the mass balance-derived dispersion in compositional analysis should mirror the dispersion observed in the black mass characterization derived. The confidence intervals of recovered F masses calculated from the raw material mass and its compositional analysis vs. mass balance derived do not overlap, indicating potential issues in F analysis (105 mg ± 32 mg vs. 195 mg ± 41 mg). It is possible that 1) LiF forms in characterization of the original sample, whereas mass balance-derived analysis includes acidic leaching and hence larger recovered F quantity, and 2) IC depends on selectivity and the speciation of F under the studied conditions is not known.

Implication to Recycling Processes

European Union is planning to introduce recovery targets for following elements in battery recycling: Li, Cu, Co, and Ni. Therefore, based on the results of the present study, it is clear that the management of F is closely linked to the management of Li: it was shown that up to 30% of Li present in the black mass could be extracted by water. Any recycling process that utilizes wet-processing prior to leaching will have to manage the generated waste waters in terms of Li recovery as the extraction to water was enough to risk not achieving the goal in the EU directive: 70% Li recovery by 2030. Furthermore, the presence of reactive F results in limited Li solubility which will make it difficult to produce concentrated Li solutions in pre-treatment stages. Clearly, further development is warranted in the battery recycling space on the management of F. It was calculated how much water would be required to wash all LiF from the material based on the observed, apparent solubility shown in Fig. 1. This is merely a best-case scenario as there exists several fluoride compounds that are less soluble than LiF in water, whose presence

would then make washing of F as a strategy prohibitively expensive. If the solubility is influenced by mostly F, then from the extraction percentages, it could be estimated that roughly $100/31.6 = 3.2$ times more water is required (i.e., $100/3.2 = 31.25$ g/L solid concentration).

The extraction results from water leaching indicated that F tends to remain in the raw material, most likely as insoluble compounds. This complicates any future recycling process as it means more aggressive chemicals will need to be utilized to extract the fluorides, creating mixed anion and metal solution streams. The F will end up in acidic leaching solution from where it potentially can end up into precipitates. For example, if Fe is removed by a process relying on pH adjustment, there could likely be co-precipitation of metal fluoride compounds in impurity removal precipitation or intermediate product precipitation. Total F extraction (sum of water and acid leaching) ranged between 98.5 and 99.7% for F and mass fractions of 68 to 382 mg/kg F were observed in leach residues. Leach residues should be treated with care as to minimize the impact of F in any potential reuse application. Finally, based on the present literature, it is not clear how F originating from LiPF₆ speciates under recycling conditions. This should be addressed by future studies in order to aid process development on F management.

The thermal decomposition behavior of LiPF₆ has been investigated by several researchers [17, 19]. A thermal treatment process aimed at thermally decomposing the LiPF₆ could potentially help alleviate the supersaturation caused by excess F present in LiPF₆ if PF₅(g) could be recovered before leaching. However, based on the reaction and despite the potential removal of PF₅(g), fluoride remains stoichiometrically bound to Li. Therefore, water-based pre-treatment processes would still cause splitting of Li stream by having present these nearly insoluble compounds. Low-temperature thermal treatment is not solution to the F issue.

In order to allow sustainable recycling of Li-ion batteries, efficient methods for removing and recovering Li from dilute sources are needed, or alternatively, techniques to separate Li selectively prior to leaching are required. As F is linked to Li content in the system as well, this directly impacts the ambitions laid in the updated draft of battery directive by European Union [29]. Good Li recovery and recycling efficiency are intrinsically linked to the recovery of F in the present-day batteries, necessitating further research and innovations on the recovery of F and Li. Either it must be accepted that F needs to be recovered in the hydrometallurgical process, or a pre-treatment process must be devised that is specifically designed to manage at minimum the fluorides in the material.

Conclusions

In this study, black mass samples originating from spent batteries were milled, water and acid leached alongside with and without reductive additives such as CoS and Al foils from the mechanical separation studies. Milling with additives was explored; however, no clear changes to crystal structure was detected. It was hypothesized that the reason was too short milling time as per the theories of mechanochemistry.

It was shown in the water and acid leaching that fluoride presents a pervasive challenge, ending up in any water stream. F was present in both water and acidic leaching solutions. Some F also remained in the leach residue (68–382 mg/kg F). No improvement in Li extraction was observed after milling in water leaching. The solubility limit of the F salts was most likely the limiting factor in water-based extraction of Li. Li and F both were dissolved at level of *ca.* 500 mg/L despite the varying black mass to water mass ratio. The solubility limit of LiF(s) has been shown by others to be *ca.* 1.34 g/L, or *ca.* 360 mg/L Li at $T = 30\text{ }^{\circ}\text{C}$ where the experiments were carried out. In the water, there was a molar excess of F ranging from 3 to 5 (F/Li ratio), further indicating LiPF_6 as the source of Li and F in water leaching. Nearly 30% of Li was extracted in H_2O leaching. It was therefore suggested that any pre-treatment process that involves water would encounter this issue of dissolving part of the F and Li, creating a dilute Li stream.

Finally, in the acidic leaching, it was shown that extraction of Ni and Mn was improved by the investigated additives (CoS and Al). Surprisingly, even under the relatively mild leaching $T = 30\text{ }^{\circ}\text{C}$ and without any external reductant, relatively high extractions for Ni, Co, and Mn were reached in the baseline experiment without pre-treatment and water leaching. This was most likely caused by the LFP cathode materials present in the raw material, an assessment which was supported by prior literature that investigated co-leaching of NMC and LFP cathodes. Although extractions appear improved (e.g., for Ni going from 78 to 96%), some uncertainty remains as to what extent the presence of LFP affected the catalytic leaching.

Overall, in light of the present results, the research on Li-ion battery recycling, considering tightening regulations, should seek solutions that would allow extraction of Li and F without creation of diluted, additional water streams or cause wastes or intermediate products to be contaminated by F.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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