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Effect of lithium ion on the separation of electrode materials in spent lithium ion batteries using froth flotation

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ABSTRACT

There is an urgent need to develop a recycling process for spent Lithium-Ion Batteries (LIBs). Amongst the various recycling technologies proposed, froth flotation is considered a cost-effective candidate for the separation of graphite from the lithium metal oxides due to the hydrophobic nature of graphite. However, experimental studies have identified that soluble lithium has a significant impact on the separation efficiency.

Two series of experiments were undertaken to understand the influence of lithium ions. The first used a semisynthetic mixture of spent anode and pure cathode material based on lithium nickel manganese cobalt oxide ($LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$) or NMC-111 cathode material. The second used mixed samples of spent lithium ion batteries of the same composition. Both the separation efficiency and the flotation kinetics are reported. The soluble lithium concentration is shown to have a significant impact on both. However, if the spent battery material is washed to reduce the lithium ion concentration, the flotation efficiency and kinetics are similar with the graphite recovery exceeding 90% and the graphite grade exceeding 84% in a single flotation stage.

1. Introduction

Li-ion batteries (LIBs) are important for many different applications such as portable electronic devices like laptops, power tools and e-mobile technologies such as bicycles and vehicles. As shown in Fig. 1, demand for these devices is expected to increase at 25% per year to 2030 [1], at which time the e-mobility sector will represent approximately 89% of the total demand. Despite the long life of LIBs, this forecast also indicates that there will be a high generation of LIB waste [2]. Therefore, recycling is a necessity due to the high content of valuable materials inside these devices such as graphite, electrolytes, base metals and cathode materials based on lithium metal oxides. If successful, battery recycling may be contributing around 7% of the raw material demand by 2030, but recycling capacity must be increased by about 25 times compared with the current capacity. The current global recycling capacity is around 322 kta in 2022 and all the installed recycling capacity is based on the use of hydrometallurgy and pyrometallurgy techniques or combination of them [3]. From all these facilities, 71% of the recycling facilities are in East Asia [3], of which 188 kta of battery recycling capacity is in China. Europe is the second highest region with an installed capacity of 92 kta. North America has a total capacity of 20 kta split between Canada and the USA.

Several recycling technologies have been proposed in order to recover the valuable materials from spent batteries for new battery manufacturing. These processes are mainly based on either hydrometallurgical technology using acid leaching coupled with a solvent extraction process. These processes generally have a high metal recovery, but also a high consumption of acid and other reagents [4]. An alternative approach is pyrometallurgy, which is attractive due to its simplicity [5], but with a high economic and environmental costs due to the high energy consumption of the process [6] and the potential generation of dangerous poly-aromatic compounds such as dioxins or hydrogen fluoride (HF). A further method is froth flotation, which is attractive due to ability to separate hydrophobic materials e.g. (graphite) from hydrophilic materials such as lithium metal oxides and metals contained in the cathode materials [7].

Froth flotation is a physicochemical process where particles with different chemical and physical properties are selectively separated

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using chemical reagents and air bubbles used as carriers. Reagents such as collectors, frothers, activators and depressants are used to either accelerate the separation or improve the separation efficiency.

Collector reagents are chemicals mainly based on nonpolar molecules such as kerosene, diesel, etc. or molecules with ionic nature such as xanthates or amines. These reagents interact chemically or physically with the particle surface, improving hydrophobicity therefore attachment onto the bubble surface. This enables these particles to be transported upward into the top of the gas-liquid phase where the interfacial energy is minimised [8].

Frothers are amphiphilic molecules, this is a chemical structure with a polar head or hydrophilic part and another hydrophobic part. Frothing agents play several roles in the separation process. They help with hydrodynamics aspects such as gas hold-up and bubble size and froth stability which is necessary to hold collected minerals but ideally this froth must be able to decay quickly to avoid problems in pumping operations [9]. Typical reagents used for this purpose include the use of aliphatic alcohols, propylene glycols and polypropylene glycol alkyl ethers.

Considering the simplicity and versatility of froth flotation technology, several research teams have proposed using froth flotation as a promising technique for the separation of anode materials from cathode materials. Several authors report a high grade of cathode materials in tailings (between 50% - 99%) and anode materials in the concentrates with grades between 75% - 85%, depending on processing conditions and the number of flotation stages. A summary of the typical processing conditions used for these materials and reported in different works is presented in Table 1.

All these reported works used spent battery materials where the extent of liberation or binder removal was not quantified [15]. It is noted that separation efficiency of the process depends strongly on the ability to liberate the electrode material from the electrodes and the organic binder. The hydrocarbon nature of the binder has potential to alter the surface properties of the cathode particles making them hydrophobic, significantly impacting the ability to separate them from graphite via froth flotation. When fully liberated battery materials are simulated by using a synthetic mixture of pure graphite and lithium metal oxides [10]. The results indicate high recoveries (greater than 99% in some cases for the anode materials) with low cathode recoveries (less than 10% in some cases), providing very positive evidence for the efficient use of flotation technology for the separation of the battery anode and cathode materials.

The effect of soluble lithium in the recovery of lithium metal oxides using froth flotation has not been explored. It has been studied in terms of risks of its accumulation and impact on the processing water after Table 1

Typically processing conditions found in flotation of spent electrode materials.

Processing Condition	Units	Value	References
Agitation Speed	rpm	900–1800	[7,10–14]
Solid Content, C _w	%w/w	4-13	
pH	[-]	9–12	
Collector Dosage	g/t	150–2000	
Frother Concentration	mg/L	8–30	
Air Flowrate	L/h	48–300	
Flotation Time	min	8–25	

many cycles of use [16]. However, within the wider field of flotation there have been several works investigating the influence of electrolytes in the foaming properties of frothers [17]. These electrolytes generally increase the ionic strength of the solution increasing froth stability, and this has been observed in tests measuring the froth height, where the froth height is increased [18]. The effect of greater froth height leads to greater draining time of water in the froth phase [19] and a lower water recovery.

The presence of lithium ions in solution is hardly surprising when considering flotation of spent LIBs. Initially lithium is present as a cathode material, but lithium ion transportation between the anode and cathode is explained via the following reversible electrochemical reactions [20].

$$\mathrm{Li}^{+} + \mathrm{C}_{6} + 1\mathrm{e}^{-} \rightleftharpoons \mathrm{Li}\mathrm{C}_{6} \tag{1}$$

$$2\text{LiMO}_2 \rightleftharpoons 2\text{Li}_{0.5}\text{MO}_2 + \text{Li}^+ + 1\text{e}^-$$
(2)

where the reaction (1) and (2) are the anodic and cathodic reactions, respectively.

This migration phenomenon is the electrochemical basis for all technological devices produced. Other new cathode technologies with a high energy density include the use of sulfur and pure lithium acting as cathode with the following anodic reaction [21].

$$\mathrm{Li}_2 \mathrm{S}_8 \rightleftharpoons \mathrm{S}_8 + \mathrm{Li}^+ + 2\mathrm{e}^- \tag{3}$$

These reactions suggest the presence of lithium ion in both the anode and cathode compartments during operation and at the end of life.

In addition to the general migration between anode and cathode, on the anode surface a complex surface layer is formed, called the solid electrolyte interface (SEI). This interface is formed on the graphite anode during the first few charging-discharging cycles. This layer permits the lithium ion transport and blocks electrons in order to prevent further electrolyte decomposition which ensures continued



Fig. 1. 2018–2030 Lithium ion battery demand (data taken from [1]).

electrochemical reactions, improving the battery life [22]. This interface is composed by partially soluble and fully soluble lithium organic oxides and inorganic salts such as lithium oxide (Li₂O), lithium carbonate (Li₂CO₃) and lithium fluoride (LiF). But the mechanisms involved in the formation of these compounds still remains only partially understood [23]. Fig. 2 illustrates this interface on the anode surface.

This paper investigates the flotation performance of anode graphite from NMC-111 cathode material in the presence of both low and high lithium concentrations. The study is divided in two parts. The first part uses a semi-synthetic mixture of spent anode and pure cathode materials (NMC-111, reagent grade). This is to simulate a flotation system with a low lithium content in solution. The second part investigates the flotation of spent battery mixtures of cathode and anode materials. This simulates a more realistic flotation system with a high lithium content in solution. Additionally to these experiments, the effect of washing the spent LIBs to remove lithium prior to flotation is reported and flotation results are compared with the other two experiments.

2. Experimental part

2.1. Materials and methods

In this study, the anode and cathode materials were taken from a spent lithium ion battery (known model and manufacturer). For comparative experiments in semi-synthetic mixtures simulating a commercial battery fully liberated, the following cathode material was used, lithium nickel manganese cobalt oxide (Li_{1.05}Ni_{0.33}Mn_{0.33}Co_{0.33}O₂), NMC-111, (>99% purity, D₅₀ = 7.5 μ m, MSE supplies, USA).

In flotation experiments, Exxol[™] D80 (industrial grade, ExxonMobil, provided by Australasian Solvents & Chemicals Company Pty. Ltd., ASCC Australia) was used as a collector for anode materials. The frother used in these experiments was Methyl-isobutyl Carbinol (MIBC), >98% purity, Sigma-Aldrich, Australia.

Table 2 details the flotation conditions used in the experiments which were kept constant for each test and were consistent with previous work [10]. For the flotation trials, a Denver cell 0.5 L (Laboratory XFD-12 Flotation Machine, China) was used.

2.2. Chemical and physical characterisation of feed materials

The chemical characterisation of feed materials being used in the flotation experiments includes the natural pH determination, particle size distribution, ICP analysis, total carbon analysis, x-ray diffraction, xray fluorescence and scanning electron microscopy.

The pH values were measured using a pH-meter, Hanna Instruments, model HI-98100.

Table 2

Processing conditions used in flotation experiments.

Processing Condition	Units	Value
Cell Volume Agitation Speed Solid Content, C _w Collector Dosage Frother Concentration Air Elowrate	L rpm % g/t mg/L L/b	0.50 900 13 500 30 160
Cell Area (Cross section)	cm ²	42.33

The particle size distribution analysis was carried out using a laser diffraction particle sizer, Malvern Panalytical, model Mastersizer 2000, UK. The technique for the analyses used was based on a dry method for all samples tested.

The elemental analysis was carried out using ICP-OES analyser, model: iCAPTM 7400 duo ICP-OES, Thermo Fisher, USA, and using reference standards for different elements and prepared in a concentration between 0 and 50 mg/L respectively.

The total carbon analyses were carried out using a CHNS analyser, Thermo Fisher Scientific, Serial Number 2019.FLS0150, Germany. These analyses were carried out using the reference compound BBOT, 2,5-bis(5-tert-butyl-2-benzoxazolyl) thiophene, analytical standard, Elemental Microanalysis, UK.

The x-ray diffraction analysis was carried out using a Rigaku benchtop powder X-Ray Diffraction (XRD) instrument, model Miniflex600, Japan. The analyses were carried out at 40 kV and 15 mA and using a copper cathode as radiation source. The XRD spectra were analysed with a 2 θ angle between 5° - 80°. Additionally, this equipment was used for detecting the change of phases in feed, concentrate and tailings in order to check the presence of oxides after the material processing using froth flotation. The XRD results were processed using the free access software Match version (3.10.2.178) for phases identification and semi-quantification of phases.

The lithium metal oxides and impurities content in feed, concentrate and tailings were quantified using an Ametek x-ray fluorescence instrument, model Spectro iQ II, USA.

The morphology of samples was studied using scanning electron microscopy (SEM). For this purpose, a JEOL JSM-7001F Schottky Emission Scanning Electron Microscope was used. Different electron micrographs were taken at different magnifications in order to observe the morphology of samples prior to flotation experiments. In this procedure, samples were stuck on the stub's surfaces using an ethyl 2cyanoacrylate adhesive. They were then dried for 48 h at room temperature and then coated with conducting carbon tape.



Fig. 2. SEI interface on the anode surface. Image taken from [23].

2.3. Preparation of feed materials

The sample preparation for the anode or mixed material was taken from a commercial spent lithium ion battery. It is summarized in the following processing flow chart (Fig. 3). Note that Case 1 are experiments where black mass samples were not washed prior to flotation experiments and Case 2 are samples washed prior to flotation experiments.

2.4. Experimental procedure of froth flotation trials

A Denver cell (Lab Denver Cell, Laboratory XFD-12 Flotation Machine, China), was used for the flotation tests, with air as the carrier gas delivered at 180 L/h. All these experiments were carried out at room temperature, this is a temperature between 15 and 20 °C. For each flotation experiment, 76 g of black mass material, in a variable composition ratio of anode (between 38 and 46%) and cathode (between 50 and 62%) was used, in experiments with just battery anode materials. These materials were placed in a 0.5 L flotation cell, together with 500 mL of pure water (Milli-Q grade). The slurry (up to 13% w/w) was stirred for 5 min at 900 rpm in order to homogenize the black mass slurry. Then, MIBC was added in order to give a 30 mg/L frother concentration in the slurry, followed by two minutes of conditioning. Then, collector was added in a dosage of 500 g/t followed by four minutes of conditioning. Finally, air was fed to the flotation cell and the flotation experiment begins.

About ten seconds after the experiment is started, the froth was recovered using a manual skimmer over 6-time intervals, it is 0.5 min, 1 min, 2 min, 4 min, 6 min and 8 min respectively. The skimming process was every 5 s for all experiments. The concentrates collected at different times enables calculation of kinetic data. Milli-Q water at pH between 11 and 11.5 (natural pH range of slurries) and using 30 mg/L of frother was added to the flotation cell as needed to keep constant the pulp level in the cell. After flotation experiment is finished, each collected fraction (concentrates and tailings) is dried at 110 °C for 18 h using a convection oven (Binder Model M 53, Germany), then all samples were weighed

using a scale (Mettler Toledo, model PE 3600, Switzerland) and then sent for sample analysis.

2.5. Characterization of the flotation products

The carbon composition for all samples collected was determined using elemental analysis (CHNS) in order to estimate the total carbon composition as graphite in samples.

Other analyses of the samples were conducted as described in section 2.2.

2.6. Flotation data processing methodology

The flotation performance for each flotation test was analysed throughout some indicators such as the flotation kinetics (for anode and cathode materials), cumulative separation efficiency (CSE) and entrainment plots. All this experimental information was based on the mass recovered and grades of anode and cathode materials in the feed, concentrates recovered at time intervals defined previously (section 2.4) and tailings.

The flotation kinetics is defined by parameters such as the kinetic rate constant (k) and the ultimate recovery (RI). They were calculated using a first-order flotation kinetic model. In this case, the flotation rate constant is modified based on the Agar model for batch flotation [24]. In this model, R is the recovery at time (t) and θ is the time correction factor as described in eq. 4.

$$\mathbf{R} = \mathbf{R}\mathbf{I}\left[1 - exp\left(-\mathbf{k}\left(\mathbf{t} + \boldsymbol{\theta}\right)\right]\right) \tag{4}$$

These parameters are obtained from the logarithmic-linear correlation given in eq. 5.

$$ln\left(\frac{\text{RI-R}}{\text{RI}}\right) = -kt + k\theta \tag{5}$$

The slope and intercept of the linear regression gives the kinetic rate constant and the intercept is related to the correction factor θ in eq. (5).

Finally, another indicator of metallurgical efficiency is the Cumula-



Fig. 3. Processing flow diagram of sample preparation.

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tive Separation Efficiency (CSE), it is calculated using the following eq. (6) [25].

$$CSE = R_v - R_g \tag{6}$$

Where R_v (%) is the recovery of the valuable material and R_g (%) is the gangue recovery at specific time.

2.7. Data reconciliation using lagrange multipliers

In the separation system, the measured grade data for each component in the system is submitted to an aleatory and systematic error. That means that the mass balance between each component is not 0. Therefore, the Lagrange multipliers methodology [26,27] was used in order to adjust the grade for each stream in the system such that the corrected mass balance is 0 for each component in the system "feed-concentratetailings". More details about this methodology applied for these experiments is found in the Supplementary Information.

3. Experimental results

3.1. Physical-chemical characterization of feed materials

Information about physical and chemical analyses carried out for all black mass samples tested can be found in the supplementary information file.

3.2. Chemical analysis of processing water after flotation experiments

Before the flotation experiments, the lithium content in the processing water was quantified using ICP analysis for lithium in solution for both series of experiments. For the semi-synthetic mixtures, the results indicated a low concentration of lithium in solution. By contrast, for the spent battery samples the results showed a much higher lithium concentration when these materials are contacted in aqueous media. However, for the Spent Battery case, the sample can be washed readily to reduce the soluble lithium concentration in the flotation media. The lithium concentration results for each case are summarised in Fig. 4.

In experiments carried out using spent anode and pure cathode material (NMC-111), one part of lithium is given by the pure cathode material and the rest by the anode material. Fig. 4 shows solubility experiments carried out using 8% solids content of cathode material in slurries. These analyses show that the pure NMC cathode material contributes around 1.58 mg Li⁺ soluble/g pure cathode, which represents around 46.69% of the total soluble lithium in the experiments with anode and pure NMC. The rest of the soluble lithium is given by the

anodic material (53.31%). These results indicate the presence of lithium ion in the anode materials which is due the migration of lithium under the normal charging and discharging of LIBs.

Similarly, in the spent battery mixed samples, one part of lithium is given by the anode material and the rest by the cathode material. The chemical analyses carried out using samples with 1% wt solids content of mixed material in slurries, indicated that the spent battery feed material releases around 16.9 mg Li⁺ soluble/g material. This is one order of magnitude higher than the semi-synthetic mixtures. Assuming the same quantity of soluble lithium comes from the anode, this is just 5% of the total soluble lithium. The remainder which is 95% of the total soluble lithium in the system is contributed from the cathode.

Additionally, in the feed spent battery mixed samples, the total lithium concentration in the sample was 4.39% wt. If this value is compared with soluble lithium found in the slurries, it means that around 34.6% of total available lithium in the material is soluble in the processing water used for froth flotation.

3.3. Flotation trials for semi-synthetic mixtures of anode and cathode materials

3.3.1. Flotation trials of semi-synthetic mixtures and spent battery mixed samples

In these trials, the composition of the feed materials is kept constant. Fig. 5 shows the recovery of anode and cathode materials versus time for the mixture 38 wt% anode material from a spent battery and 62 wt% pure cathode material. Each green line (anode recovery) is paired with a pink line (cathode recovery). These lines represent the average of experiments carried out in duplicate.

The standard deviation (σ_{Exp}) for anode recovery and cathode recovery given in the table inset is low, indicating a good reliability for these experiments. The results show a high recovery of the anode material (graphite) for both sets of experiments with semi-synthetic mixtures and the spent battery materials. For the anode recovery (oxides) the aim is to have as low a recovery possible and it can be seen that the recovery is much lower in semi-synthetic samples, compared with spent battery mixed samples.

Despite these differences, the difference in terms of recovery at eight minutes of flotation time for anode and cathode materials indicates a good separation efficiency. The rate of flotation shown by the slope of the lines indicates that the spent battery mixed materials have faster kinetics for both the anode and cathode materials.

Fig. 6 shows the entrainment plot of the cathode recovery versus the water recovery for the experiments analysed in Fig. 5. Results indicated a linear shifted up entrainment curve [28]. This is a set of linear curves



Fig. 4. Lithium content in solution for the experiments studied.



Fig. 5. Flotation kinetics for anode and cathode materials.



Fig. 6. Entrainment plot for materials essayed.

below the identity line y = x, which indicates the main flotation mechanism is water entrainment and not by true flotation of the material itself. Results with spent battery samples indicate a higher entrainment of oxides up to 7 times higher in terms of the oxide recovery compared with the results using semi-synthetic mixtures. As mention previously, a higher oxide recovery in the concentrate is detrimental, because it reduces the grade (purity) of the concentrate.

Fig. 7 shows a comparative analysis of cumulative grade versus cumulative recovery for the flotation trials carried out. These results indicate a highly efficient separation for the semi-synthetic mixture with a grade of 87% at the maximum graphite recovery. By contrast, the Spent Battery mixed samples give a much lower concentrate grade which drops to as low as 66% at the maximum anode recovery. This is due to the high content of cathode materials entrained in the concentrate.

3.3.2. Effect of lithium removal on the separation of spent battery materials In these series of flotation experiments, a spent battery mixture of electrode materials taken from a spent lithium ion battery were tested in the presence of a high and low lithium content in solution. The composition of the feed or black mass being separated was variable. This was a mixture of 38–46 wt% anode material and 50–58 wt% cathode material, the residual 4% of mass were impurities present in the material, including heavy elements such as copper and light elements like lithium and aluminium. The processing conditions used in these experiments were the same used in the flotation trials with semi-synthetic mixtures, i.e. methyl-isobutyl carbinol (MIBC) as frother and ExxolTM D80 as collector. For experiments with a low lithium concentration in solution, samples were washed previously with deionised water in 3 stages in order to maximise the lithium removal.

Fig. 8 shows the flotation kinetics of the anode and the lithium metal oxides in the presence of a high and low lithium concentration in solution. Like Fig. 5, these results show that the fastest graphite recovery occurs when lithium is present in a high concentration compared to lithium at lower concentrations due to washing. In terms of recovery at 8 min of flotation time, graphite recovery for both tested conditions are



Fig. 7. Cumulative grade versus cumulative recovery for anode concentrates.



Fig. 8. Flotation kinetics of anode and oxide after roasting and re-roasting.

similar. In terms of oxide recovery, a high lithium concentration increases the oxide recovery in concentrates, which is negative in terms of quality of graphite concentrates.

Fig. 9 shows the entrainment plot of the cathode material recovery versus the water recovery. Results indicate that when black mass samples are washed prior to flotation, the lithium removal substantively affects the entrainment of oxides to the froth. It is quantitatively based on the linearity of these plots and verified because entrainment factor (slope) and true flotation (intercept) of the oxides or cathode material decrease compared with experiments without prior washing of samples.

In Fig. 10, the cumulative grade versus cumulative recovery plot indicates a quantitative improvement in the separation curve when the black mass material is washed prior to flotation with similar results obtained with semi-synthetic mixtures. These results, suggests that lithium removal from the flotation system is critical in order to minimise the oxide entrainment to the froth and achieve better grades of graphite concentrates. At the same time this phenomenon suggests that the presence of lithium salts also affects the quality of the froth.

4. Discussion

In the experiments carried out using semi-synthetic mixtures and spent battery samples without and with water washing prior to flotation, the Cumulative Separation Efficiency (CSE) is analysed after 8 min of flotation.

In Fig. 11, CSE results indicate that in samples with a high content of lithium in the flotation media, the separation is not efficient with low values of CSE. By contrast, when samples are washed, the CSE increases greatly, achieving values close to those for the semi-synthetic mixtures which are fully liberated and have a low lithium content in solution.

Figs. 12 and 13 show the kinetics plots for the anode and the cathode in all experiments studied. These curves are obtained by fitting the anode and cathode recoveries (Figs. 5 and 8) to eq. (5) to obtain the kinetic parameters, it is the ultimate recovery (RI) and the kinetic rate constant. The regression constants are given in the table within each figure. Fig. 12 indicates fast flotation kinetics for the anode material in experiments with a high lithium concentration. By contrast, when



Fig. 9. Entrainment plots for unwashed and washed samples.



Fig. 10. Cumulative grade versus cumulative recovery for anode concentrates.

lithium is in lower concentrations the kinetics are slower. Theta values (θ) found for these experiments using eq. 5, indicate a small positive correction for the anode material. This means that the anode begins to float even before air is introduced into the flotation cell.

For cathode materials, Fig. 13, shows a linear trend regarding to the rate of recovery these materials. They show different recoveries depending on the lithium concentration such as indicated by the values of ultimate recovery (RI). From these values, the semi-synthetic mixture presents the lowest value, instead the spent battery sample unwashed, presents the highest value of ultimate recovery. When lithium is removed from the flotation system by washing, the ultimate recovery decreases, but not up to values observed for semi-synthetic mixtures. This indicates the effect of the residual binder on the cathode materials, impacting negatively the oxide recovery.

In Fig. 14, if values of RI from the kinetic analysis for the anode and cathode in each experiment are compared, the lithium content in solution does not affect the ultimate recovery (RI) of graphite. Instead, values of ultimate recovery for oxides are strongly correlated with the

lithium content in solution. This phenomenon could be explained by the froth stability influenced by the lithium content. Several studies on the effect of dissolved salts in flotation report the frothing effect of salts [29,30]. Similarly, it has been shown that the saline content impacts the water drainage time of froths [31,32]. If water entrainment is the main mechanism of oxide recovery in graphite concentrates, then the presence of high concentration of lithium causes the froth to retain more oxides.

In terms of entrainment factor and true flotation values for each experiment tested, these values are represented by the slope and intercept in entrainment plots and for this analysis, these values were taken from Fig. 6 and Fig. 9 respectively for all materials tested. From this analysis, the synthetic mixture offers the lowest true flotation value for the cathode material with a low entrainment factor (0.39% and 0.15) (Fig. 15). By contrast, the unwashed spent battery mixed material shows the highest values of true flotation and entrainment factor (7.18% and 0.55), which is related to the highest lithium concentration. Instead, when lithium is removed from processing water, the values of true



Fig. 11. Separation efficiency for samples tested with and without washing.



Fig. 12. First order rate plot for anode materials.

flotation and entrainment factor decrease considerably to 0.15% and 0.26, respectively.

An additional point is related to the potential loss of soluble lithium either from washing or as a consequence of flotation. As has been observed, soluble lithium plays an important role, because this ion impacts negatively the purity of the graphite concentrates. The problem can be solved by washing the samples with water in order to remove the soluble lithium. This pretreatment stage increases considerably the quality of the graphite concentrate with graphite grades over 84% purity, similar to graphite concentrates in fully liberated semi-synthetic samples. Additionally, this pretreatment stage generates waste solutions with a high lithium concentration. Extraction of lithium from the wastewater should be considered for improving the environmental and economic feasibility of the process.

One final point is the use of flotation reagents to improve the kinetics and separation efficiency of the separation process. These frothers and collectors like the lithium ions will be ultimately discharged in the wastewater. However, these reagents are organic compounds that are readily broken down in aeration water treatment processes. The quantities involved are orders of magnitude lower than the reagents used in the alternative processes such as acid leaching.

5. Conclusions

In this study, semi-synthetic mixtures of anode taken from a commercial spent battery and NMC-111 cathode material and mixed spent battery samples from spent lithium ion batteries have been separated using froth flotation in a batch flotation cell. Promising results have been achieved for all experiments carried out. The main conclusions from this work are the following:

- 1. In semi-synthetic samples completely liberated, anode materials are able to be separated efficiently from cathode materials in one rougher stage.
- 2. For spent battery samples the flotation results give less efficient separation compared to semi-synthetic mixtures, if there is no washing prior to flotation.
- 3. Spent Battery mixed samples washed to reduce the lithium concentration exhibit a better performance in terms of separation efficiency.



Fig. 13. First order rate plot for cathode materials.



Fig. 14. Values of RI for anode and cathode for each experiment.

- 4. The soluble lithium content in spent battery samples plays an important role in the cathode recovery. It confirms that entrainment by water recovery is the main mechanism for cathode materials reporting to the concentrate which in turn impacts negatively on the concentrate grade.
- 5. When materials are washed prior to flotation, the soluble lithium is removed from the materials. As a consequence, this pre-treatment minimises the oxide recovery and it increases considerably the quality of graphite concentrates with grades over 84%. Despite these good results, in order to obtain a graphite purity greater than 90% additional cleaning flotation stages will be needed.

As lithium is an essential component of LIBs, a loss of lithium into the wastewater is both economically and environmentally undesirable. Considering this problematic, lithium can be recovered using precipitation stages using phosphates salts in order to generate insoluble lithium phosphate [33]. Other techniques involve the use of lithium solvent extraction processes [34] or the use of ionic exchange resins [35]. This issue should be an important consideration in the continued

development of LIB recycling using froth flotation as the separation process.

Author contributions

Luis Verdugo: conceptualization, experiments, data processing and writing; Jorge Menacho: methodology and reviewing; Warren Bruckard: methodology, experiments and reviewing; Andrew Hoadley: Supervision; Lian Zhang: Supervision; Barbara Etschmann: experiments, methodology and reviewing. All authors of this article have read and agreed to the published version of the manuscript.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Luis Verdugo reports equipment, drugs, or supplies was provided by Australasian Solvents & Chemicals Company. Luis Verdugo reports equipment, drugs, or supplies was provided by Envirostream Australia



Fig. 15. Entrainment factor versus collector dosage for each experiment.

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Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2023.123241.

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