A REVIEW OF HYDROMETALLURGICAL FLOWSHEETS CONSIDERED FOR THE TREATMENT OF BLACK MASS

By

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ABSTRACT

Recycling of lithium-ion batteries has generated significant attention in recent years due to the increase in demand of EV's. This paper focusses on the hydrometallurgical treatment of the black mass stream produced from the battery shredding operations. Many flowsheet configurations exist and are reported by recycling companies. Typically, flowsheets can be characterized by a) complete metal separation via solvent extraction, electrowinning and/or crystallization operations and b) direct production of battery pre-cursor material. This paper will provide a review of some of the flowsheets considered by current companies and will comment on feed characterization, leach chemistry, SX circuits considered and product recovery circuits.

Keywords: black mass, cobalt, nickel, lithium, sodium sulphate

INTRODUCTION

SGS Canada is a leading supplier of testing services to the mining and metallurgical industries and operates metallurgical laboratories out of Canada, Chile, Mexico, South Africa and Australia. Several clients of SGS (such as Neometals, Aleon Renewable Metals, Coherent Corporation, and H.C. Starck Tungsten) are existing battery recycling firms or are developing technologies to support battery recycling. While researching the overall industry it became apparent that many technologies exist for the hydrometallurgical treatment of black mass. The authors therefore decided to document their review and presented their work to the EV Battery Recycling and Re-use Conference held in Detroit(1) in March 2023. This paper provides further detail and information to this review. The review is not intended to be exhaustive but does show the wide variety of process routes under current consideration.

The use of lithium-ion batteries (LIBs) is expected to increase in the near future due to the increased use of electric vehicles (EVs), which use LIBs as the power source. Figure 1 shows the predicted sales of EVs and the EV market penetration up to 2035. LIBs are also widely used in portable electronic devices (e.g. cellular phones and laptops). The popularity of LIBs is due to their high energy density, high voltages and low weight-to-volume ratio. With the increased usage of LIBs comes the requirement to recycle these batteries. Current feedstock to recycling facilities consists to a large extent of manufacturing scrap (cell or precursor cathode active material, pCAM), and a lesser extent of End-of-Life (EOL) batteries. As the usage of LIBs increases and more EOL LIBs become available, the feedstock to recycling facilities is expected to change from off-spec (i.e. scrap) to EOL material as is shown in Figure 2. As battery chemistries are changing rapidly due to ongoing developments of new batteries with improved performance or due to metal shortages (i.e. cobalt), it is safe to assume that the metal ratios (Ni:Co:Mn) contained in EOL batteries are significantly different from what may be the primary battery chemistry at the time of recycling.

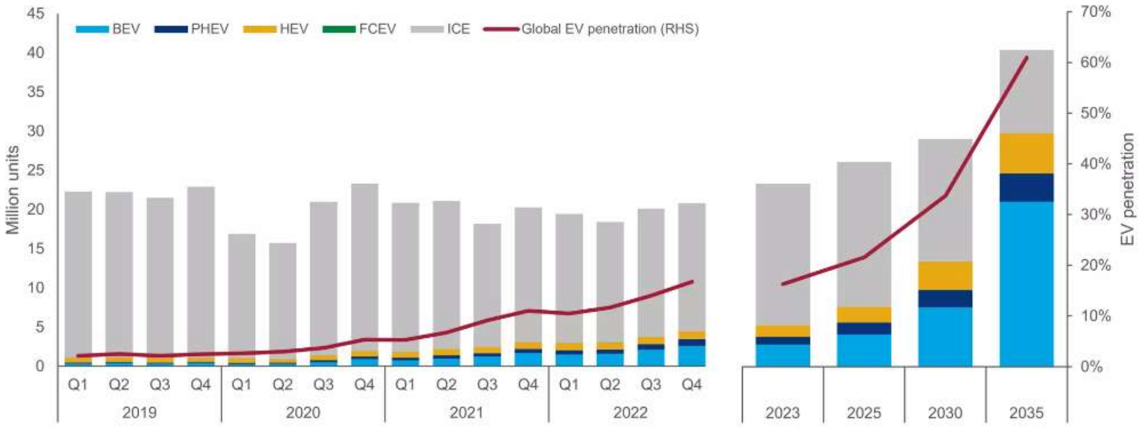

Figure 1 Vehicle Sales Forecast(2)

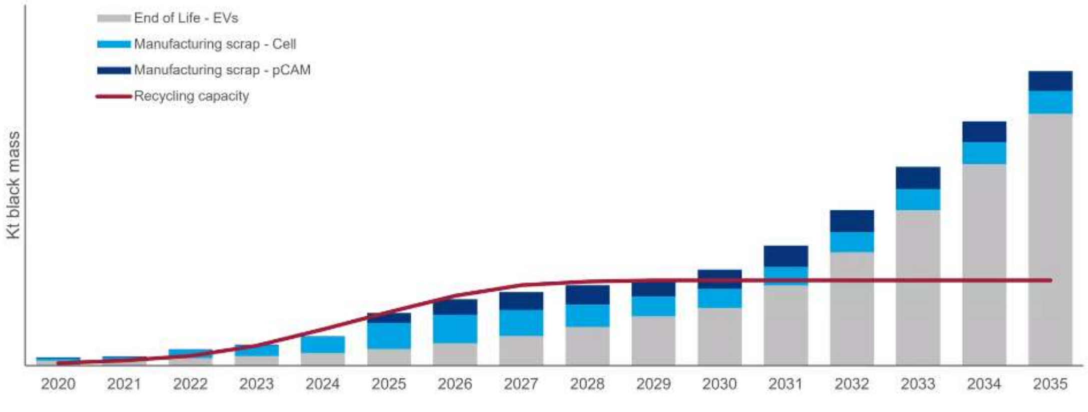

Figure 2 Feedstock and Recycling Capacity in North America(2)

Conceptually, a typical battery recycling flowsheet consists of a mechanical step (shredding) where plastics are separated from the metallics (aluminum and copper foils) and the black mass.

Duessenfeld(3) reports that around 57% (see also Figure 3) of their input LIB mass consists of black mass. This paper focusses on the hydrometallurgical treatment options of the black mass stream.

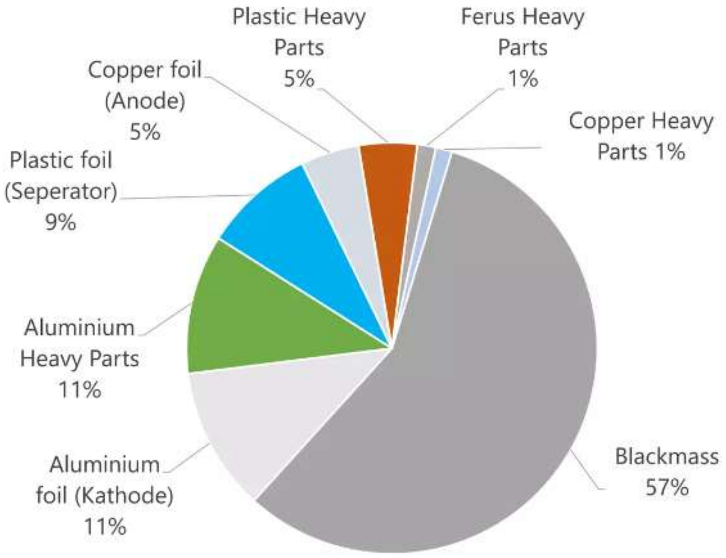

Figure 3 Duesenfeld Mechanical (shredding) Output(3)

BLACK MASS FEED CHARACTERISATION

1.1 Components of LIBs

LIBs consist of various components as shown in Figure 4. The general design of a LIB cell consists of a copper foil current collector, a porous anode which is made of graphite, a porous separator comprised of polypropylene or polyethylene, a porous cathode consisting of active material mixed with conductive carbon and a polymeric binder such as polyvinlylidene fluoride (PVDF) and an aluminum foil current collector. The porous anode, porous cathode and separator are soaked in an electrolyte solution which consists of a lithium salt (such as $LiPF_6$, $LiBF_4$, $LiCF_3SO_3$ and $Li(SO_2CF_3)_2$) which is dissolved in a mixture of organic solvents. Some organic solvents which are typically used are dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), ethylene carbonate (EC), cyclohexylbenzene, polypylene carbonate (PC) diethyl carbonate (DEC), dimethyl sulfoxide (DMSO)(4)(5).

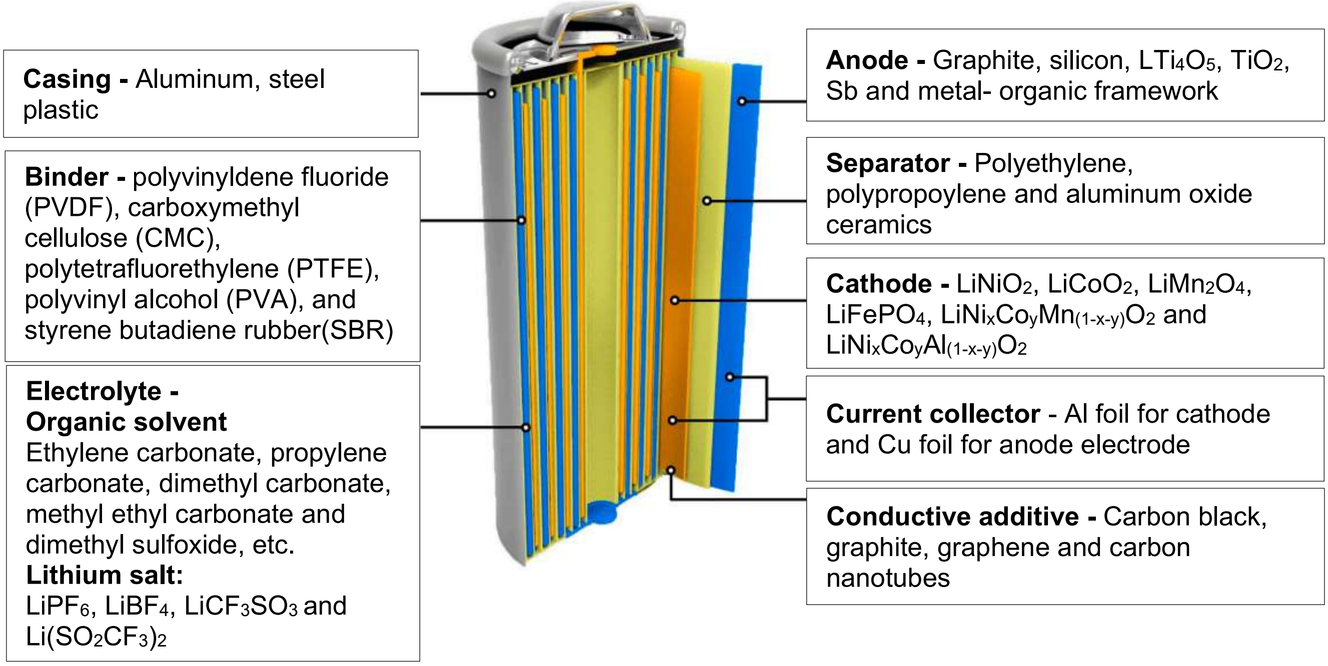

Figure 4: Structure of typical cylindrical LIB(6)

1.2 Black mass processing steps

The spent LIBs are first subjected to discharging and dismantling before various stages of mechanical recovery. However, before the mechanical separation, the LIBs can be subjected to pyrolysis. Pyrolysis is a process whereby the black mass is heated to temperatures of approximately 500-700°C after separation from the shredded material to remove the electrolyte components via thermal decomposition(7). During the pyrolysis process, the fluorine-containing components are removed. The mechanical recovery stages can include dry crushing, drying sieving, and sorting(8).

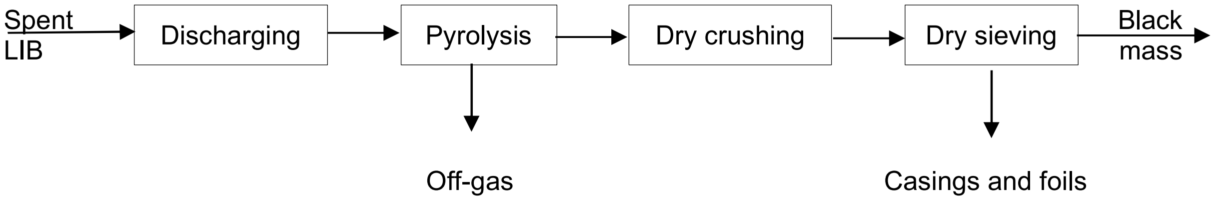

Figure 5: Production of black mass

1.3 Composition of black mass

The black mass is a combination of cathode and/or anode electrode powders which consist of lithium metal oxides, lithium iron phosphates (cathode) and graphite (anode). A list of the major cathode chemistries for LIBs is detailed below(9)(10):

1. $LiMn_2O_4$ - Lithium manganese oxide (LMO)
2. $LiFePO_4$ - Lithium iron phosphate (LFP)
3. $LiNi_{0.3}Mn_{0.3}Co_{0.3}O_2$ - Lithium nickel manganese cobalt oxide (NMC111)
4. $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ - Lithium nickel manganese cobalt oxide (NMC622)
5. $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ - Lithium nickel manganese cobalt oxide (NMC811)
6. $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ - Lithium nickel cobalt aluminium oxide (NCA)
7. $LiNi_{0.5}Mn_{0.3}Co_{0.1}O_2$ - Lithium nickel manganese cobalt oxide (NMC532)
8. $LiCoO_2$ – Lithium cobalt oxide (LCO)

Table 1 below shows the detailed analyses of black mass samples which SGS is currently working on. The composition of the black mass can be classified as containing either high cobalt or high nickel-containing samples. The composition of cobalt ranges from 17-22% Co for the high cobalt samples and the composition of nickel ranges from 13- 17% Ni for the high nickel samples. The Li content ranges from 3.0- 3.7% Li for all black mass samples. Typical moisture content is 2-5% and particle size ranged from a fine K80 of ~ 30 µm to a K80 of several 100 µm.

Table 1: Detailed chemical analyses of different black mass samples

	High cobalt				High nickel	
Element	Black Mass 1 %	Black Mass 2 %	Black Mass 3 %	Black Mass 4 %	Black Mass 5 %	Black Mass 6 %
Ni	6.79	5.09	6.58	10.6	17.0	12.83
Co	17.1	22.1	21.2	18.6	3.67	4.46
Mn	4.65	3.14	3.68	2.89	3.02	4.19
Li	3.39	3.32	3.36	3.74	3.11	3.03
Cu	0.22	1.18	0.55	0.72	1.38	2.37
Zn	-	-	0.03	0.01	<0.004	0.006
Fe	0.10	0.68	0.37	0.21	0.04	0.03
Al	2.50	2.04	1.21	1.54	1.42	0.5
Ca	0.04	0.28	0.12	0.05	0.02	0.02
Mg	0.04	0.14	0.24	0.10	0.01	0.01
Na	0.06	0.28	0.06	-	0.05	0.06
Cr	0.01	0.04	0.003	0.00	<0.00	0.002
C	38.4	26.4	36.8	37.0	45.5	47.8
F	-	-	1.62	1.75	2.48	2.05

RECYCLING PROCESS CONSIDERATIONS

As illustrated in this paper, many processing routes exist for the treatment of black mass streams. While this paper focusses on the hydrometallurgical treatment, it should be noted that dedicated pyrometallurgical processes have also been developed for the treatment of black mass. A good example is Umicore's operation in Hoboken (Belgium) which operates a 7000 t/a facility with stated plans to expand.

Most of the hydrometallurgical flowsheets incorporate a reductive leach process using sulphuric acid and hydrogen peroxide, though some exceptions exist such as the chloride based flowsheet described by Ehren(11). Hydrogen peroxide is both a reductant (to reduce the $LiNi_xCo_yMn_{(1-x-y)}O_2$) and an oxidant (to oxidize the metallic copper foil). All flowsheets include one or several steps to remove impurities such as copper, fluoride, iron, aluminum, zinc and manganese.

Many flowsheets under consideration lead to the production of sodium sulphate as a waste or by-product. Sodium sulphate is produced when soluble metals are loaded (SX) or precipitated using sodium-based chemicals. Two moles of NaOH are required to load or precipitate one mole of nickel. Taking the Black Mass Sample 5 from Table 1, one can calculate that around 2.4 tonnes of $Na_2SO_4.10H_2O$ or 1.0 tonne of Na_2SO_4 is produced for each tonne of black mass processed. While salt splitting (into dilute NaOH and H_2SO_4) is a viable technical option, this is still considered an expensive option. Therefore, the use of ammonia (NH_4OH) is considered a potentially viable alternative and leads to the production of ammonium sulphate which can be a feed source in the fertilizer industry.

The recycling projects reviewed for this paper can be grouped as follows:

- Complete separation of metals (Mn | Co | Ni | Li)
- Direct production of battery precursor material (MnCoNi | Li).

Complete separation of metals is usually accomplished via solvent extraction and/or electrowinning and can be used to produce a metal sulphate crystal or metal cathode. When individual metal sulphates are produced, these require further treatment for the production of cathode active materials, including blending of sulphate salts in the correct ratio, dissolving these in water and reacting the metal sulphate liquor with sodium hydroxide or sodium carbonate to produce solid metal hydroxide or carbonate and sodium sulphate(12). Therefore, the production of an intermediate metal product requiring re-dissolution and reaction with a sodium-based reagent will lead to additional production of sodium sulphate (in addition to the sodium sulphate produced during the processing of black mass). Flowsheets capable of producing a mixed metal hydroxide without an intermediate will therefore lead to lower production of sodium sulphate.

There are several entry points to the LIB recycling business. Types of companies include dedicated recycling companies (with IP, such as Li-Cycle and others), automotive and battery companies, chemical reagent companies (such as Solvay) and trading companies. It is also worth noting that while mining projects employ mining guidelines and regulations, especially relating to public disclosure (TSX, ASX, etc.), recycling projects do not share the same industry guidelines. They are in effect chemical plants. Mining projects offer the opportunity to dispose of or store waste streams in dedicated tailing storage facilities (TSF). Recycling projects typically do not offer such opportunities.

BLACK MASS TREATMENT FLOWSHEETS

Complete Separation (Mn | Co | Ni | Li | Na/NH_4)

Li-Cycle, Lithion, Neometals and the Veolia-Solvay JV all have in common that complete separation of Mn, Co, Ni and Li is targeted. All four projects use a sulphuric acid / hydrogen peroxide based leach flowsheet to produce a pregnant leach solution and a graphite based leach residue, but differ from one another on how the pregnant leach solution is treated. Table 2 summarizes the liquor treatment unit operations and the sections below provide additional detail.

In all cases presented here, additional treatment will be required to produce precursor cathode active material from metal sulphate or metal products. The additional treatment is likely to consist of blending, water leaching (sulphate salts) or acid leaching (metal) followed by neutralization with NaOH or Na_2CO_3 to produce metal hydroxides or carbonates and sodium sulphate.

Table 2: Summarized Unit Operations – Complete Separation Mn | Co | Ni | Li | Na/NH_4

Company	Leach Chemistry	Copper Separation and Recovery?	Impurity (FeAl) Removal	NCM Separation / Recovery Process	NCM Products	Waste alkali?	Lithium Recovery and Product
Li-CyCle	H_2SO_4/H_2O_2	CuS / CuSX-EW	Precipitation (NaOH, lime) of $Al(OH)_3$, $Fe(OH)_3$	Sequential SX of Mn, Co and Ni, with $MnCO_3$ precipitation from MnSX strip and metal sulfate crystallization from CSX and NSX strip liquors	Separate $MnCO_3$, $CoSO_4.7H_2O$, $NiSO_4.6H_2O$	$Na_2SO_4.10H_2O$	Li_2CO_3 Precipitation with Na_2CO_3
Lithion	H_2SO_4/H_2O_2 (internal recycled MnO_2 and Al powder)	CuS (Na_2S or H_2S)	Precipitation (NaOH) of $Al(OH)_3$, $Fe(OH)_3$	Column SX. CoMnSX (Cyanex 272) to separate CoMn | LiNi. Loaded organic is scrubbed with strip liquor bleed. CoMn are stripped together with pH 1 H_2SO_4. Cobalt is electrowon from CoMn strip liquor producing Co Metal (cathode) and MnO_2 (anode). Spent electrolyte is returned to stripping. Nickel is precipitated with NaOH from the CoMnSX raffinate to produce $Ni(OH)_2$	Co Metal, MnO_2, $Ni(OH)_2$	$Na_2SO_4.10H_2O$ fed to electrolysis (production of H_2SO_4 and NaOH)	Li_2CO_3 Precipitation with Na_2CO_3
Neometals	H_2SO_4/H_2O_2	CuSX (LIX84I). Salting out Crystallization of CuSO4.5H2O from strip liquor via addition of H2SO4	Precipitation of $Al(OH)_3$, $Fe(OH)_3$ with NH_4OH and oxidant (if required for oxidation of Fe_2 to Fe_3)	CoMnSX (Cyanex 272 / Ionquest 801 / D2EHPA) is used to separate CoMn|LiNi. Mn is extracted from CoMnSX Strip lIquor with Co preloaded organic (D2EHPA). Co-preloading is done by contacting stripped organic with purified cobalt stream. Final product liquors are crystallized to $CoSO_4.7H_2O$ and $MnSO_4.H_2O$ CoMnSX raffinate advances to NiSX (LIX84I or Versatic 10), with crystallization of $NiSO_4.6H_2O$ from strip liquor	Separate $MnSO_4.H_2O$, $CoSO_4.7H_2O$, $NiSO_4.6H_2O$	No. Production of Ammonium Sulphate	NiSX raffinate is treated by IX to remove divalents. LiSX (Cyanex 936, 926, 923, LIX54, LIX55, Mextral 54-100 or mixtures) to separate Li|NH_4. Li strip liquor treatment to produce final Li product (Li_2SO_4 liquor)
Solvay / Veolia	H_2SO_4/H_2O_2 (Solvay Interox Technology)	CuSX (Acorga), IX, CuEW. Production of Cu Cathode	Precipitation of $Al(OH)_3$, $Fe(OH)_3$ with NaOH or NH_4OH	Impurity SX (D_2EHPA) to separate CuFeAlMn | CoNiLi. Co SX (Cyanex 272) to separate Co | Ni Li. Crystallization of $CoSO_4.7H_2O$ NiSX (Versatic 10)) to separate Ni | Li Na/NH_4. Crystallization of $NiSO_4.6H_2O$	Separate $CoSO_4.7H_2O$, $NiSO_4.6H_2O$	unknown which alkali is used	LiSX (Cyanex 936P) to separate Li|Na/NH_4. Li strip liquor treatment to produce final Li product (LiOH / Li_2CO_3)

Li-Cycle

Li-Cycle is a Canadian-based company that focusses on LIB resource recovery and recycling. LIB recycling at Li-Cycle is a patented(5) process which involves various hydrometallurgical steps. The processing plant is expected to have a capacity of 35 000 tonnes of black mass per year and once fully operational is expected to produce lithium carbonate (8500 tonnes/annum), nickel sulphate (48 000 tonnes/annum) and cobalt sulphate (7500 tonnes/annum) [8]. Li-Cycle uses a hub and spoke model with a central hub (Rochester, NY) plant processing black mass produced at several spoke sites spread out over North America.

A simplified block flow diagram for the hydrometallurgical Li-Cycle process is illustrated in Figure 6 below. The BFD is an interpretation of the published patent and investor presentations(13) and generally follows a conventional metal separation flowsheet. The reagents in red text are possible reagents which can be used in the process plant, however, the actual process may employ a variation of the reagents listed above.

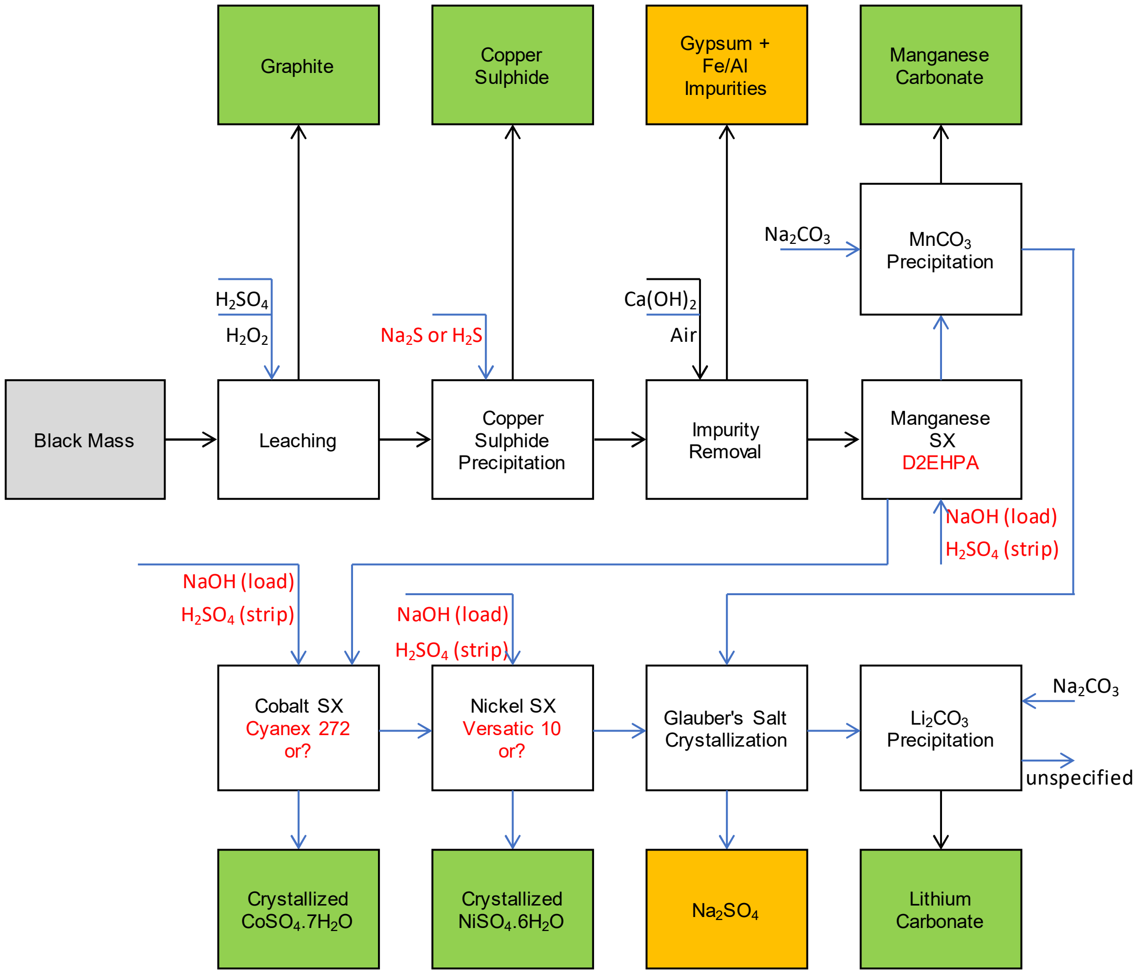

Figure 6: BFD for hydrometallurgical treatment of black mass – Li-Cycle

The pregnant leach solution (from a sulphuric acid/hydrogen peroxide leach) is subjected to copper sulphide precipitation using precipitants such as sodium sulphide or hydrogen sulphide. The solution is further purified removing iron and aluminum and based on the published production of gypsum it is assumed that calcium-based reagents such as lime are used. Of the projects reviewed, Li-Cycle is the only project using calcium-based reagents and producing gypsum. Presumably, this is driven by the improved fluoride removal performance when CaF_2 is produced.

After iron and aluminum removal the solution then undergoes manganese solvent extraction, presumably using D2EHPA. The manganese can be stripped from the organic extractant using sulphuric acid. The manganese in the loaded strip liquor is then precipitated using sodium carbonate to form a manganese carbonate. The raffinate produced from manganese solvent extraction advances to cobalt solvent extraction. Cyanex 272 is believed to be used as an extractant to extract Co from nickel, lithium and sodium contained in the Mn raffinate stream. Cobalt loaded organic is stripped using sulphuric acid and the resultant loaded strip liquor is crystallized to form cobalt sulphate. Cobalt raffinate is then subjected to nickel solvent extraction presumably using Versatic 10 to separate nickel from sodium and lithium sulphate. Sulphuric acid is used to strip the nickel loaded organic phase and the resultant loaded strip liquor is crystallized to produce nickel sulphate. Sodium sulphate is removed from the system via Glauber's salt crystallization. The mother liquor produced after crystallization is then processed to produce lithium carbonate via precipitation using sodium carbonate.

The assumed use of D2EHPA in the Li-Cycle flowsheet ensures that the liquor advancing into cobalt and nickel solvent extraction is clean and impurities such as zinc should be picked up as well. The use of calcium in impurity removal is surprising as it leads to the production of gypsum, but also produces a gypsum saturated liquor advancing into the D2EHPA SX circuit. While D2EHPA is able to extract calcium, removal is typically not quantitative and extracted calcium can lead to gypsum precipitation in scrubbing and stripping when sulphuric acid is used.

Li-Cycle has reported that the Rochester hub is on track for commissioning in 2023, with 90% of process equipment ordered and 65% of detailed engineering completed(14).

Neometals

Neometals is an emerging, battery materials producer and has developed a proprietary hydrometallurgical process for the recycling of EOL LIBs. The process is looking at the recovery of valuable materials from consumer electronic batteries (lithium cobalt oxide cathodes) and nickel-rich electric vehicle and stationary storage battery chemistries (lithium-nickel-manganese-cobalt cathodes)(15). Based on the patent by Beer(16) and other publications(17), a simplified block flow diagram of the Neometals LIB recycling process has been drawn up and is shown in Figure 7. The Neometals flowsheet was piloted at SGS Canada in 2019-2020.

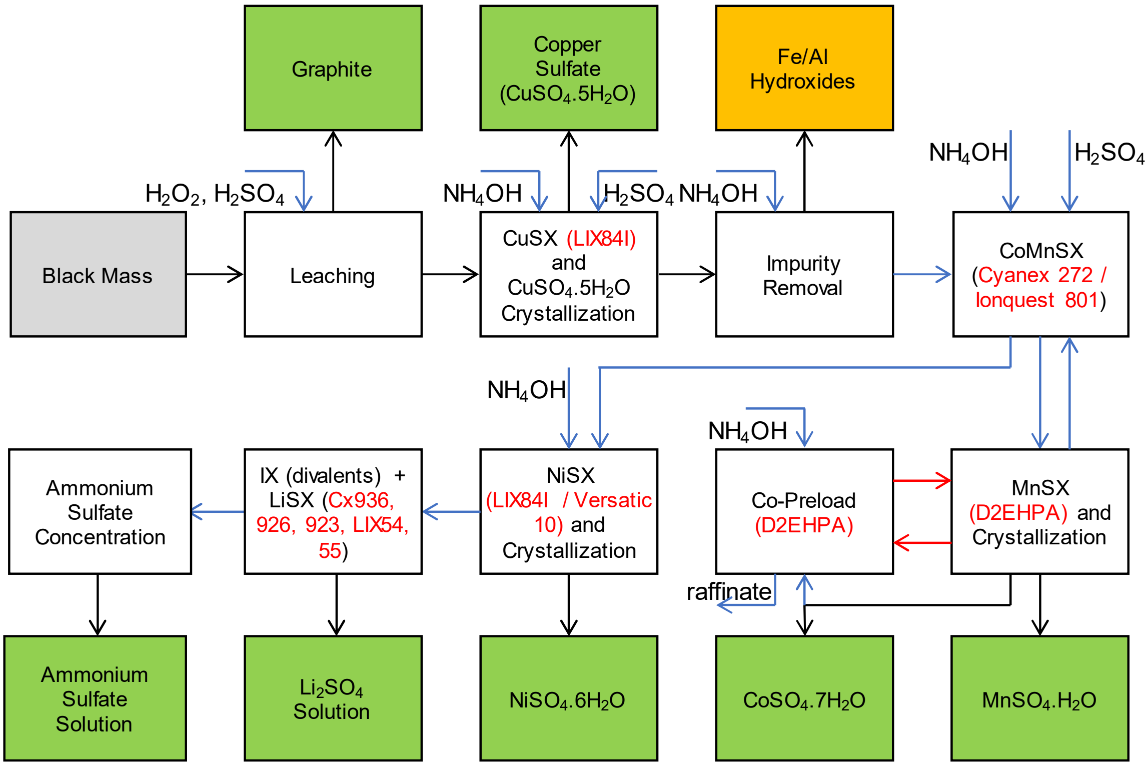

Figure 7: BFD for hydrometallurgical treatment of black mass – Neometals

In the Neometals hydrometallurgical flowsheet, sulphuric acid is used in combination with hydrogen peroxide to leach the black mass, leaving graphite in the leach residue. The pregnant leach solution is subjected to copper solvent extraction. A copper extractant such as LIX84-I (as identified by Beer(16)) can extract copper at relatively low pH values and could be a possible copper extractant used in the process. The copper is stripped from the organic phase and the loaded strip liquor is then crystallized to form copper sulphate crystals. The raffinate produced from the copper solvent extraction step is then subjected to iron and aluminum removal via hydroxide precipitation using ammonium hydroxide. After iron and aluminum removal the solution is then subjected to cobalt and manganese solvent extraction, extracting both cobalt and manganese by a single extractant such as Cyanex 272, Ionquest 801 or PC88-A(16). Both cobalt and manganese are stripped from the organic phase. Manganese is then extracted from the loaded strip liquor using a cobalt loaded extractant such as D2EHPA and is stripped using sulphuric acid. Thereafter the strip liquor advances to manganese sulphate crystallization. The purified manganese SX raffinate is split into two streams. A portion of the stream is recycled to cobalt pre-loading and is loaded onto D2EHPA, the second portion of the stream advances to cobalt sulphate crystallization.

The raffinate stream produced from the combined manganese cobalt SX advances to nickel solvent extraction. Typical nickel extractants such as LIX 84-I and Versatic 10 are possibly used as extractants for nickel solvent extraction. The nickel is stripped off the organic phase and the loaded strip liquor is subjected to nickel sulphate crystallization. The raffinate solution produced after nickel solvent extraction is further purified using ion exchange to remove divalent impurities. Lithium is recovered via solvent extraction from the purified solution. Possible extractants for lithium recovery are Cyanex 936, 926, 923, LIX 54 and LIX55. The raffinate obtained from lithium solvent extraction is directed to a step whereby the ammonium sulphate is preconcentrated.

While the operation of multiple sequential SX circuits can be challenging and carry-over of organic should be avoided, Neometals plans to use activated carbon coalescers to avoid extractant carry-over from circuit to circuit. The Neometals circuit is unique in that it avoids the production of sodium sulphate and uses ammonia in place of sodium-based reagents. Consequently, ammonium sulphate is produced as a potential feed source for the fertilizer industry. Care must be taken to avoid the formation of nickel ammonium sulphate double salts in nickel solvent extraction circuits using ammonia.

Lithion

Lithion is a battery recycling company located in Canada. The company has developed patented(18) technology for LIB recycling and commissioned an industrial-scale demonstration plant in January 2022. The capacity of its first commercial scale plant is expected to be 7500 metric tonnes per annum(19). Lithion's goal is to install more than 20 recycling plants over the next 15 years. The Lithion hydrometallurgical flowsheet consists of leaching, impurity removal, upgrading and electrowinning as shown in Figure 8.

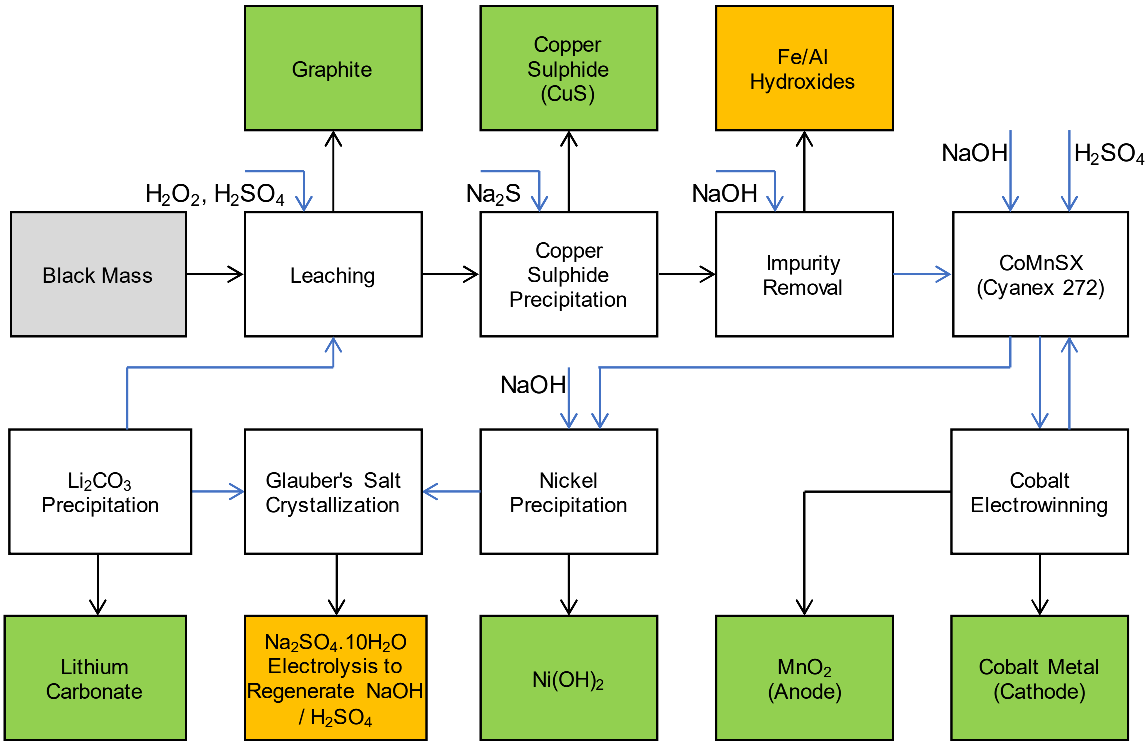

Figure 8: BFD for hydrometallurgical treatment of black mass – Lithion

The pregnant leach solution (after H_2SO_4/H_2O_2 leaching) is subjected to copper sulphide precipitation using sodium sulphide. The copper free solution is then passed to impurity removal where sodium hydroxide is used to remove iron and aluminium via hydroxide precipitation. The purified solution is subjected to solvent extraction where cobalt and manganese are extracted together using Cyanex 272 as the extractant. The loaded organic phase is stripped and the loaded strip liquor is passed onto an electrowinning step, where cobalt metal is plated at the cathode and manganese oxide is produced at the anode. The raffinate stream produced from CoMn SX is then subjected to nickel hydroxide precipitation using sodium hydroxide as a precipitant. After the nickel is removed sodium sulphate is formed via Glauber's salt crystallization. The hydrated sodium sulphate is subjected to electrolysis to produce sodium hydroxide and sulphuric acid for recycling. Lithium carbonate is precipitated from the mother liquor.

The use of electrowinning to separate cobalt from manganese is energy efficient as the same electric current is used to reduce cobalt to cobalt metal at the cathode and for manganese oxidation (to Mn^{4+}) at the anode. According to the published patent, the electro-separation of cobalt and manganese is performed in an undivided cell, which may lead to reduced efficiencies since optimal conditions (pH, temperature, current density) for cobalt electrodeposition and MnO_2 precipitation are different. Moreover, suspended MnO_2 particles could be incorporated into the cobalt deposit.

Solvay-Veolia

In 2020(20) Solvay and Veolia announced their partnership on a circular economy consortium to offer new solutions that promise better resource efficiency for critical metals used in lithium-ion electric vehicle (EV) batteries. Solvay & Veolia have not published specific information on the hydrometallurgy process, except for a simple description(21) which forms the basis of the BFD shown in Figure 9.

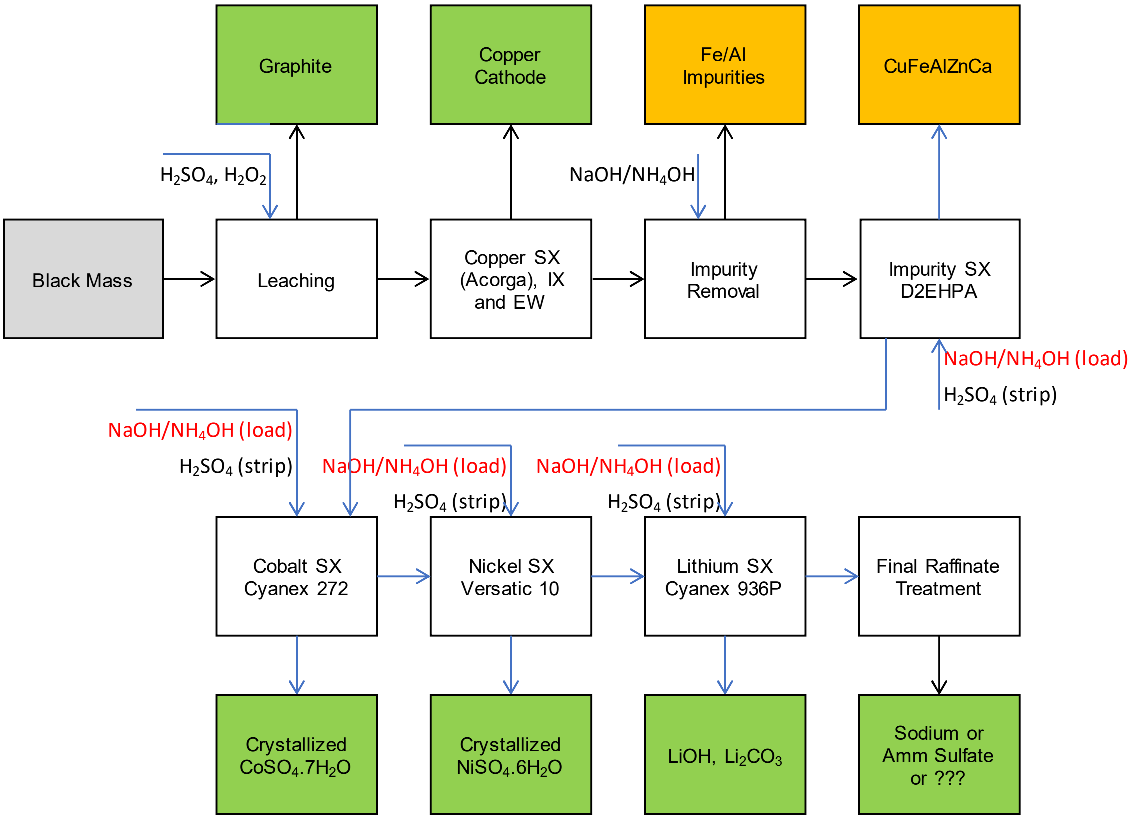

Figure 9: BFD for hydrometallurgical treatment of black mass – Solvay/Veolia

Sulphuric acid in combination with hydrogen peroxide is used to leach the black mass. The pregnant leach solution is subjected to various impurity removal and upgrading steps via solvent extraction. Throughout the flowsheet, Solvay solvent extraction reagents are used to separate each metal:

- Acorga to extract copper
- D2EHPA to extract manganese (and presumably impurities such as zinc)
- Cyanex 272 to extract cobalt
- Versatic 10 to extract nickel
- Cyanex 936 to extract lithium.

Sodium hydroxide or ammonium hydroxide are possibly used as pH modifiers. Depending on the reagent used either a sodium sulphate or ammonium sulphate stream is produced as a by-product of the process. As stated above the operation of multiple sequential SX circuits using all different reagents can be complex and care must be taken to avoid organic carry-over from one circuit into the other.

Separation using electrowinning

Various companies are proposing to use electrochemistry as a basis to separate and it is worthy to mention even though little information is provided publicly.

Aqua Metals is a US based company headquartered in Reno, Nevada and has its origins in lead battery recycling and holds several patents(22) related to its AquaRefining^{TM} technology, based on the use of methane sulfonic acid as a solvent. Aqua Metals has indicated it has filed a provisional patent, also using AquaRefining technology, for recovering high-value metals from recycled lithium-ion batteries. It is noted that the authors of this paper were not able to locate this provisional patent. Aqua Metals provided a simplified BFD (shown in Figure 10) of its proposed process at a recent conference in the USA(23). It is worth noting the less than common order of metal recovery: copper – lithium – nickel – cobalt – manganese.

Figure 10: Block Flow Diagram – Aqua Metals(23)

Partial Separation (Mn Co Ni | Li | Na/NH$_4$). Direct Production of Precursor Material

NorthVolt, Coherent Corporation and RecycLiCo all have in common that partial separation of Mn, Co, Ni and Li is targeted, producing a mixed metal hydroxide, carbonate or battery precursor material directly from black mass leach liquors offering the advantage of reduced production of waste products such as sodium sulphate. A variation of this process route appears to be applied by Redwood Materials which has indicated it produces a mixed Ni/Co sulphate product stream, which will require additional processing (and associated production of sodium sulphate) for direct production of battery precursor material. Not all leach chemistry details are available for these projects, but Northvolt, RecycLiCo and Redwood appear to use a sulphuric acid based leach flowsheet with reductants to produce a pregnant leach solution and a graphite based leach residue. Each differs from one another on how the pregnant leach solution is processed. Table 2 summarizes the liquor treatment unit operations and the sections below provide additional detail.

Table 3: Summarized Unit Operations – Partial Separation Mn Co Ni | Li | Na/NH$_4$

Company	Leach Chemistry	Copper Separation and Recovery?	Impurity (FeAl) Removal	NCM Separation / Recovery Process	NCM Products	Waste Alkali	Lithium Recovery and Product
Northvolt	H_2SO_4/H_2O_2	CuSX	Precipitation (NCM Hydroxide) of $Al(OH)_3$, $Fe(OH)_3$	Metal salts (sulfates or hydroxides) are added to adjust NCM ratio. NCM are precipitated together with NaOH. Minimim co-precipitation of impurities (Li,P,F, Mg, Na, Ca) due to use of concentrated liquors. Filtrate contains unprecipitated NCM and impurities	Battery Precursor Material ($NiCoMn(OH)_2$))	$Na_2SO_4.10H_2O$	Li_2CO_3 Precipitation with Na_2CO_3
Coherent	not disclosed	not disclosed	not disclosed	NCM are precipitated simultaneousy	cathode precursor	not disclosed	not disclosed
RecycLiCo	$H_2SO_4/SO_2/Al$	assumed grouped with Impurity Removal	Precipitation of Fe/Al hydroxides with recycled LiOH	Precipitation of Mixed (NiCoMn) hydroxide/carbonate with Li_2CO_3.	Mixed metal hydroxide/carbonate	N/A. LiOH and Li_2CO_3 used throughout	Electrodialysis to produce LiOH and H_2SO_4 for recycle
Redwood	H_2SO_4/Reductant	CuSX, $CuSO_4$	not disclosed	While undisclosed, it is assumed that SX with H_2SO_4 strip is applied	Mixed Ni/Co Sulphates	not disclosed	Li_2SO_4

Northvolt

Northvolt is a Swedish battery developer and manufacturer, specializing in lithium-ion battery technology for electric vehicles. Northvolt has a factory in Skellefteå, northern Sweden, part of Northvolt's plan to increase production capacity to 32 gigawatt-hours by 2023. Its headquarters for research and development is in Västerås, Sweden. Northvolt has developed LIB recycling technology in-house and its technology is patented(24).

The Northvolt hydrometallurgical flowsheet consists of leaching, copper removal, impurity removal, NMC ratio adjustment, NMC precipitation, residual NMC precipitation for internal recycling, Glauber's salt crystallization and lithium recovery as lithium carbonate. A simplified block flow diagram is shown in Figure 11.

Northvolt uses a reductive acid leach with sulphuric acid and hydrogen peroxide to produce a PLS rich in Ni, Mn, Co and Li as well as impurities such as Cu, Fe, Al, F and Zn. Copper contained in the

PLS is recovered via SX-EW or IX. The copper free solution is then passed to impurity removal where recycled NMC hydroxide is used to remove iron and aluminum via hydroxide precipitation. While not explicitly identified one of the patent examples also used IX to control impurities such as zinc.

The concentration of Ni, Co and Mn in the purified solution is subsequently adjusted by the addition of individual metal sulphate salts to a total metal concentration of 1.55 mol/L and the ratio of Ni:Co:Mn in the target precursor material. NMC is subsequently precipitated together using NaOH (the patent also identifies LiOH and NH_4OH). The inventors(24) claim that by adjusting (i.e. increasing) the metal concentration, selectivity against key impurities is introduced during NMC precipitation at relatively low pH. This leaves unprecipitated Ni, Co and Mn in the filtrate together with ionic impurities. The residual NMC is precipitated with NaOH and recycled upstream (acid neutralization, impurity removal). After the NMC is removed sodium sulphate is formed via Glauber's salt crystallization. Lithium carbonate is precipitated from the mother liquor.

Within a separate patent(25) co-authored by Northvolt personnel, a variation of the Northvolt process route is described. The process variation is based on solvent extraction and crystallization of metal sulphates from strip liquors. Residual metal contents in the crystallizer mother liquor are subsequently precipitated and returned upstream as a source of alkalinity in precipitation circuits.

Since battery precursor material is produced directly from black mass leach liquor, the overall production of the waste stream (in this case sodium sulphate) is reduced. However, due to the need to adjust the NMC ratio by the addition of individual nickel, cobalt or manganese sulphates, individual separation of these metals on a fraction of the overall metal stream will still be required.

The use of NMC hydroxides in impurity removal may lead to NMC metal losses, since impurity precipitation is typically carried out at pH 3-5, a range where the re-dissolution of metal hydroxides is slow.

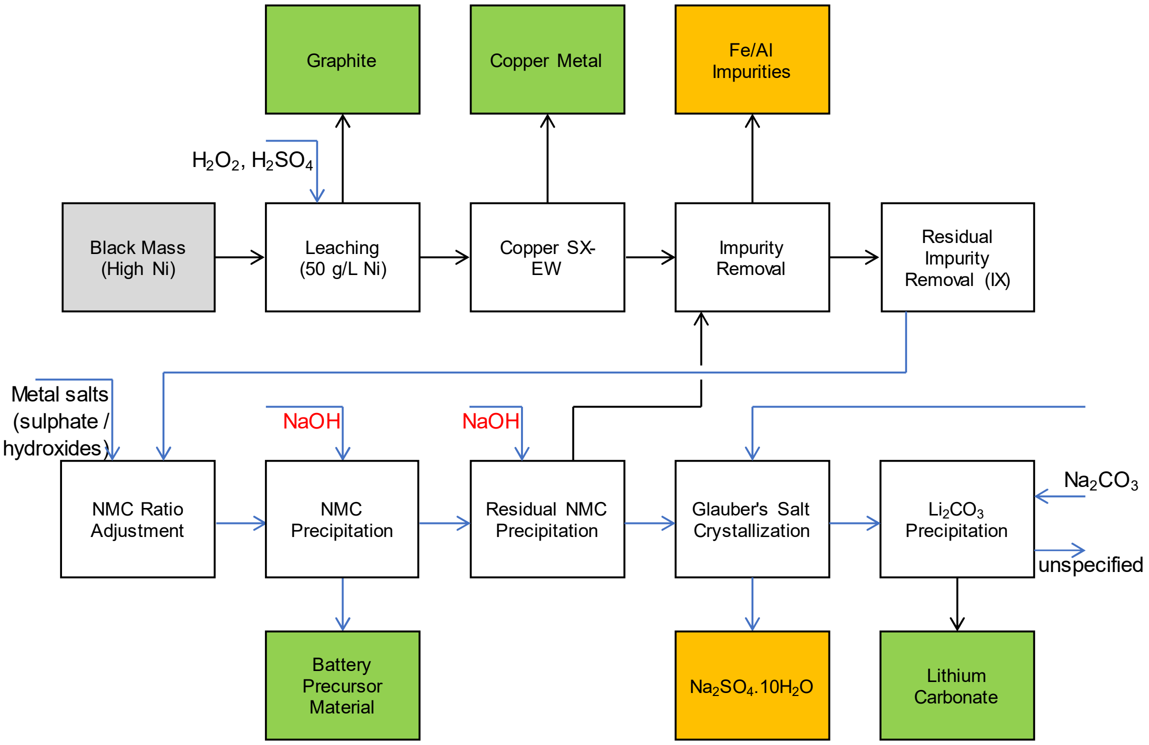

Figure 11: BFD for hydrometallurgical treatment of black mass – Northvolt

Coherent

Coherent Corporation (formerly II-VI Incorporated) is an American manufacturer of optical materials and semi-conductors and is head quartered in Saxonburg, Pennsylvania. Coherent has developed a Streamlined Hydrometallurgical Advanced Recycling Process (SHARP) described in a white paper by Nazari(26). While the white paper does not reveal much process information, it describes a hydrometallurgical process consisting of black mass leaching, impurity removal and direct production of battery precursor material. A simple conceptual BFD is shown in Figure 12.

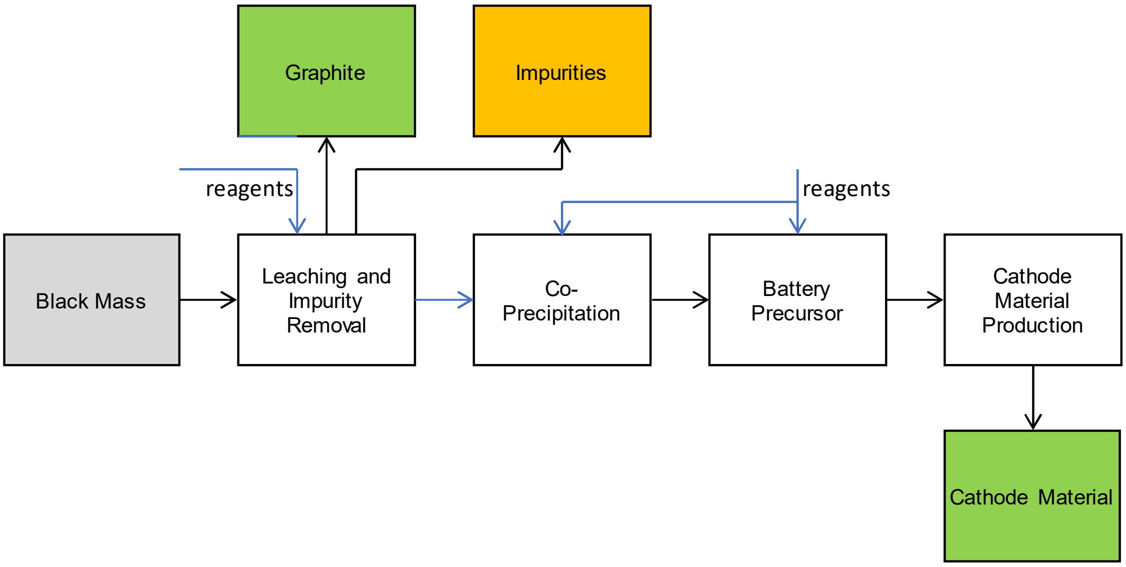

Figure 12: BFD for hydrometallurgical treatment of black mass – Coherent

RecycLiCo

RecycLiCo, formerly known as American Manganese, is a publicly-traded company listed on the TSX venture exchange. The company has developed and patented(27) technology for the recycling of battery cathode waste. The technology has been described in several journal articles(28)(29). Combined these sources of information form the basis of the flowsheet description below (Figure 13). RecycLiCo recently announced that its demo plant has operated for "thousands of person hours" producing battery grade lithium carbonate and high nickel pCAM(30).

Jung et al(29) describe a reductive sulphuric acid leach process using SO_2 gas as reductant. Typical leach conditions included 10% solids, 0.8M H_2SO_4 and SO_2 addition to ORP of 350 mV leading to metal extractions of over 99%. The authors opined that leaching with SO_2 resulted in a much smaller volume of leachate than leaching with H_2O_2. Impurities are removed via the addition of recycled LiOH and NMC were precipitated together with Li_2CO_3 (presumably also recycled internally). While the authors looked at precipitation with LiOH, it was found that this was not practical due to the high resulting dilution when 1M LiOH is used. In place of LiOH, the authors used Li_2CO_3. The authors reported that a 177% stoichiometric addition of Li_2CO_3 was required to recover over 99.5% of contained nickel and cobalt and that the final Ni/Co precipitate containing elevated levels of Li_2CO_3 indicating poor reactivity of the Li_2CO_3 used.

The nickel and cobalt free filtrate containing 10 g/L Li advances to lithium electrodialysis in a three-compartment cell to regenerate LiOH and H_2SO_4. When operated at a current density of 204 A/m^2, 0.8 M LiOH was generated in a single pass.

The RecycLiCo process appears able to process black mass, producing precursor material directly without the production of sodium sulphate due to the internal recycling of LiOH and Li_2CO_3 formed by electrodialysis of Li_2SO_4. Obvious concerns exist around the cost of operating the electrodialysis cell. High recycling rates of LiOH and poor utilization of Li_2CO_3 will contribute to increased electrical costs.

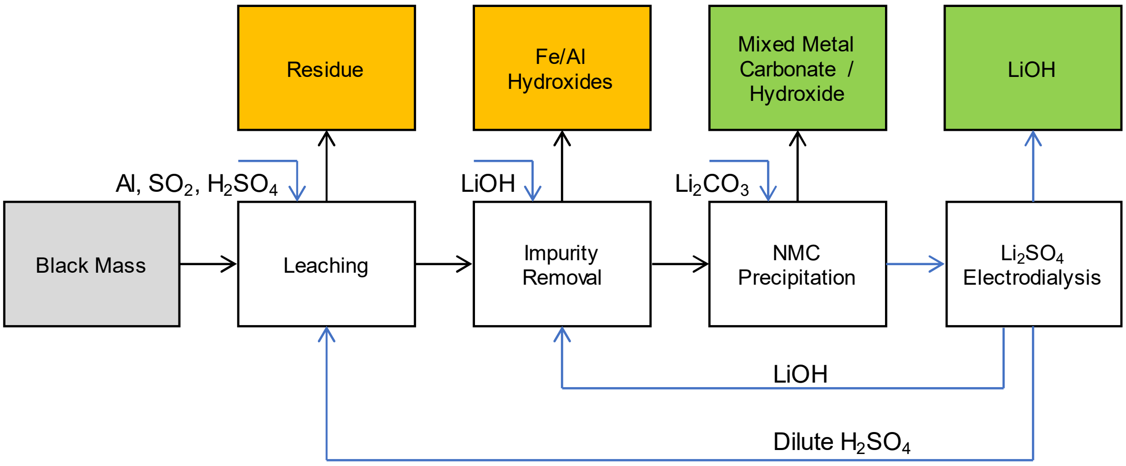

Figure 13: BFD for hydrometallurgical treatment of black mass – RecycLiCo

Redwood Materials

Redwood Materials is an American company headquartered in Carson City, Nevada. The company aims to recycle LiBs and produce battery materials for electromobility and electrical storage systems. Not much information on its processing flowsheet is available publicly except for what is posted online(31). A simple conceptual BFD is shown in Figure 13. The flowsheet indicates the separate production of copper sulphate, mixed nickel/cobalt sulphate and lithium sulphate. This implies that a sulphate based leach process is used and that solvent extraction with sulphuric acid stripping is employed to produce separate copper and mixed nickel/cobalt streams. The production of an intermediate sulphate stream also implies that additional processing steps (water leaching, neutralization with NaOH, production of Na_2SO_4) are required to produce precursor cathode active materials. Insufficient detail is provided to comment on the behavior of impurities within this flowsheet.

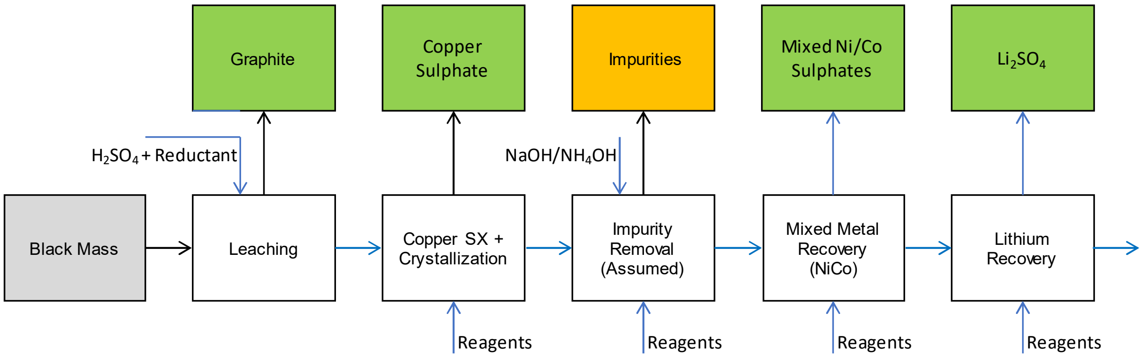

Figure 14: BFD for hydrometallurgical treatment of black mass – Redwood Materials

FINAL THOUGHTS: ISSUES, OPPORTUNITIES AND CONCLUSIONS

The developments in battery chemistries are rapid and technologies developed today for the treatment of current battery chemistries need to be able to adapt quickly to changing feedstocks. While the current recycling need is primarily for off-spec material, this will change to end-of-life materials.

While this review is far from exhaustive and other authors have provided significantly more comprehensive reviews(32)(33), it is clear that developments are rapid and not all developments reported in this or other papers will have a successful outcome. The companies must conduct thorough and rigorous testing (including pilot and demonstration style piloting) to evaluate the robustness and operability of the processes developed and their ability to handle constantly changing feedstocks.

The ability to produce precursor cathode active material directly is of interest, as it provides the opportunity to limit the production of waste streams such as sodium sulphate. However, this means that the recycler needs to continuously adapt its process to meet the ever-changing battery chemistry needs.

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