Green Chemistry – Critical Review

The Importance of Design in Lithium Ion Battery Recycling – A Critical Review

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Supplementary information

The data in **Table 3** were taken from the literature.[1] Eight pilot scale processes were identified for which most of the mass and energy data were available for LIB recycling from shredded material. These are listed in **Table S1**, with the flow sheets shown in **Figures 1-8**. All processes use a similar selection of lixiviants, with a range of different processing conditions such as time, temperature and solid to liquid ratio. The cost of dissolution is given as a ratio normalised to the least expensive method, and the potential value of the product is also presented as a ratio, normalised to the least expensive digestion stage (omitting recovery costs). Input material for each process is defined as one of the following:

- *Cathode black mass* – comprising of the active material, binder and conductive additive (the current collector has been removed by means of chemical or mechanical delamination);
- *Cathode calcined black mass* – comprising of the active material only (the black mass has been calcined at high temperatures to remove the binder and conductive additive);

both of which contain Al impurities.

Table S1: Summary of chosen hydrometallurgical processes from literature.				
Process no.	**Pre-treatment**	**Dissolution process**	**Recovery process**	**Literature reference**
1	Discharge, disassembly, crushing, cathode separation	Reductive leaching	Co-precipitation after calibration of Co, Mn and Ni	Kim *et al.*[2]
2	Crushing, wet scrubbing and drying	Reductive leaching	Precipitation of Mn and Fe, solvent extraction of Cu and Co, precipitation of Co	Dutta *et al.*[3]
3	Discharge, disassembly, cathode separation	Reductive leaching	Co-precipitation	Gao *et al.*[4]
4	Provided by e-waste centre in China	Reductive leaching	Flotation and precipitation	Huang *et al.*[5]
5	Shredding, sieving, drying and calcining (500 °C for 1 h)	Electrochemical leaching	Electrowinning of Mn and Co	Prabaharan *et al.*[6]
6	Crushing, sieving, grinding, alkaline leaching, reduction roasting, carbonated water leaching	Leaching	Evaporation of Li filtrate, solvent extraction of Ni, Co and Mn	Hu *et al.*[7]
7	Discharge, disassembly, separation, cathode calcining (600 °C)	Reductive leaching	Co-extraction of Mn, Co and Ni, co-precipitation of Li and co-precipitation of NMC	Yang *et al.*[8]
8	Wet shredding, flotation, sieving, calcining (500 °C for 1 h)	Leaching	Precipitation of Co and Mn	Barik *et al.*[9]

When recycling processes are reported in the literature, details of the criteria are often omitted (e.g. recovery efficiency of metals that are deemed ‘economically unimportant’ to the process). Therefore, the following selection criteria, assumptions and caveats have been made:

- Since the batteries treated are of LMO/NMC chemistry, chemistries of only LFP, NCA and LCO were omitted. Mixtures of LIBs that include LMO or NMC are included.
- The following parameters for each process are assumed to remain the same after scaling to 1 kg of starting material:
    - Temperature;
    - Acid and reducing agent concentrations;

    - Solid to liquid ratio for leaching;
    - Leaching time.
- Prices of chemicals are taken as a mean from a range of suppliers of chemicals listed on Alibaba.com and converted to £ per kg, or £ per L, to enable direct comparison (see **Table S3**).
- Water prices are based from household prices, not business prices.
- Calculations include the time taken to heat the reaction vessel to the desired temperature, assuming a standard heat source, but it is assumed that the reaction vessel is fully insulated and requires no additional costs for heat losses.
- If a purity range is given for a chemical, then the median purity is taken.
- By-products from the removal of small amounts of impurities are omitted from net values.
- Labour and equipment costs are omitted from all processes.

The solvent volume required to fulfil the S/L ratio was calculated with **Equation 1**. The volumes of reducing agent and acid required were calculated using the concentration used in the process and the stock concentration, shown in **Equation 2**. The price of the reducing agent and acid used was calculated in **Equation 3**, based on the density of the chemical in question if necessary. For processes 5, since the reducing agents were electrolysis (6.5 kWh for dissolution and recovery, accounting for 2/3 and 1/3, respectively), costs for electricity consumption during dissolution were calculated in **Equation 4.** The remaining water required was calculated in **Equation 5**, and price calculated using **Equation 3**. The time required to heat the solvent to the desired temperature was calculated using the heat capacity of water, as shown in **Equation 6**. The cost to heat the solvent to the desired temperature was calculated by **Equation 7**. The total leaching expenditure was therefore the sum of:

- Acid price;
- Reducing agent price;
- Water price;
- Time to reach desired temperature.

The relative cost was then calculated by dividing each calculated cost by the cheapest value, in this instance the HCl leaching process 8.

The mass of an element recovered was calculated using the leaching efficiency, recovery efficiency and metal content in the original leach feed, shown in **Equation 8,** followed by calculation of moles. Leaching efficiencies are shown in **Table S2**. The mass of the final product was calculated by addition of the mass of the element and mass of the ligand. The mass of the ligand in the product was calculated by using the ratio of moles of the element: moles of ligand, and molar mass of the ligand. For processes that yield intermediates such as $NMC(OH)_2$ as well as Li products, the moles of Li for LiNMC and Li products (e.g. Li_2CO_3) were calculated accordingly depending on moles required to form LiNMC (with the remaining moles used to calculate the mass of the other final Li product). For process 2, $CoSO_4$ and Co were quoted as products, but since Co was produced on a much smaller scale and a ratio was not provided, Co was omitted from calculations. Recovery efficiencies for Li and Mn were not provided, so an assumption of 80 % was made in this case. For process 4, the ratio of MnO_2 and Mn_2O_3 was not stated, so a 50:50 assumption was made. For processes 5 and 8, leaching and recovery efficiencies were not provided for Li, so an assumption of 80 % was made. For process 7, mixed hydroxides were produced but no value or product was stated and so this was omitted. For process 8, Mn oxides were produced, but again no value or product was stated. Therefore, a 50:50 mixture of MnO_2 and Mn_2O_3 was assumed. The value of the product was calculated using the product mass (kg) and product price (£/kg), and the net value calculated by taking away the cost of dissolution from the value of the product. In this case the net value does not include recovery costs (e.g. precipitation). The relative value was then calculated by dividing each calculated value by the HCl leaching process 8 value.

Table S2: *Leaching efficiencies of Li, Ni, Mn, Co, Al, Cu and Fe from 8 hydrometallurgical processes in the literature.*

	Leaching efficiency (%)						
Process no.	**Li**	**Ni**	**Mn**	**Co**	**Al**	**Cu**	**Fe**
1	98	98	98	98	89	-	-
2	99	-	99	97	-	97	-
3	100	50	62	37	4.5	-	-
4	92	-	90	-	-	-	92
5	-	-	99	99	-	99	-
6	85	99	99	99	-	-	-
7	-	99	97	99	-	-	-
8	-	-	99	99	-	-	-

The data in **Table 4** were obtained from empirical experiments to delaminate NMC from the Al current collector (cathode), or delaminate graphite from the Cu current collector (anode). Samples of Nissan Leaf electrodes were treated in a selection of the most common solvents used in the literature, along with a solvomechanical process in development at the University of Leicester. The processed samples were then rinsed with deionised water and dried in air, before being weighed to determine how much material was recovered, and how much material (if any) was leached into solution. The space-time-yield and efficiency were calculated from these values, and a relative cost calculated with respect to HCl using the values in **Table S3**, as was done for the eight literature processes in **Table 3**.

Treatment of the cathode:

- *Sulphuric acid*: The cathode was leached in 1.0 M H_2SO_4 at room temperature with no agitation, until complete delamination occurred after 5 hours. Approximately 33 wt.% of the sample was dissolved, containing a mixture of all metals present.
- *Hydrochloric acid*: The cathode was leached in 1.0 M HCl at room temperature with no agitation, until complete delamination occurred after 60 minutes. Approximately 39 wt.% of the sample was dissolved, containing a mixture of all metals present, including the entirety of the Al current collector.
- *Sodium hydroxide*: The cathode was leached in 0.5 M NaOH at room temperature with no agitation, until complete delamination occurred after 30 minutes. Approximately 2 wt.% of the sample was dissolved, containing only Al from the current collector.
- *NMP*: The cathode was placed into a bath of NMP at room temperature with no agitation, until complete delamination occurred after 15 min. Approximately 3 wt.% of the sample was dissolved, with no metal detected in the leachate, i.e. mass loss is that of the PVDF binder alone.

Table S3: Sources and prices of chemicals and commodities utilised in the TEA.		
Item	**Price (£/$)**	**Source**
Exchange rate	0.7864	XE Currency Charts, https://www.xe.com/currencycharts/?from=USD&to=GBP&view=1Y, [accessed 10/06/2020]
Item	**Price (£/kWh)**	**Source**
Electricity	0.14	https://www.theecoexperts.co.uk/solar-panels/kwh-electricity-prices [accessed 03/04/2020].
Item	**Price (£/L)**	**Source**
Household water	0.001	Severn Trent, non-potable wholesale rate, 2018/19
Item	**Price (£/kg)**	**Source**
$Al(OH)_3$ (99.6 %)	0.55	Alibaba, https://www.alibaba.com/product-detail/Industrial-Grade-Aluminium-Hydroxide-Powder_62338205442.html?spm=a2700.galleryofferlist.0.0.54ab1a51N1WaQf&s=p [accessed 10/06/2020].
Co (99.95 %)	47.10	Alibaba, https://www.alibaba.com/product-detail/Cobalt-Metal-for-chemicals_62308133488.html?spm=a2700.galleryofferlist.0.0.678dc2c7dRe3RG&s=p [accessed 10/06/2020].
$CoCO_3$ (99.8 %)	51.03	Alibaba, https://www.alibaba.com/product-detail/Factory-Offer-Best-Price-Cobalt-carbonate_60523686896.html?spm=a2700.galleryofferlist.0.0.604616d98tjKtg [accessed 10/06/2020].
$CoSO_4 \cdot 7H_2O$ (98 %)	5.89	Alibaba, https://www.alibaba.com/product-detail/Colbalt-Sulphate-CoSO4-7H2O-Cobaltous-Sulphate_60566986825.html?spm=a2700.galleryofferlist.0.0.1a3d7d27P7ya83 [accessed 10/06/2020].
$Cu(OH)_2$ (98 %)	3.53	Alibaba, https://www.alibaba.com/product-detail/98-Copper-hydroxide-Cudroxtechnical-CAS-20427_62058871232.html?spm=a2700.galleryofferlist.0.0.360414a6WCQOuB&s=p [accessed 10/06/2020].
$CuSO_4$ (99 %)	4.55	Alibaba, https://www.alibaba.com/product-detail/Export-Industrial-Grade-99-High-Purity_60792636776.html?spm=a2700.galleryofferlist.0.0.1ed91effiVLw9P&s=p [accessed 10/06/2020].

$FeCl_3$ (96 %)	20.41	Alibaba, https://www.alibaba.com/product-detail/FeCl3-Ferric-chloride-CAS-7705-08_62170198321.html?spm=a2700.galleryofferlist.0.0.32275e7ciuE93J&s=p [accessed 10/06/2020].
$Fe_2(SO_4)_3$ (97 %)	2.36	Alibaba, https://www.alibaba.com/product-detail/Ferric-Sulfate-Fe2-SO4-3-manufacturer_60207249706.html?spm=a2700.galleryofferlist.0.0.36d9330bMxag4n&s=p [accessed 10/06/2020].
Formic acid (24 M)	0.37	Alibaba, https://www.alibaba.com/product-detail/producer-leather-dyestuff-chemical-high-purity_62027325995.html?spm=a2700.galleryofferlist.0.0.4e3f7d06PnIkUW [accessed 10/06/2020].
Hydrochloric acid (12 M)	0.17	Alibaba, https://www.alibaba.com/product-detail/Transparent-Liquid-Hydrochloric-Acid-31-32_60241244897.html?spm=a2700.galleryofferlist.0.0.21222c51gpF0tb&s=p [accessed 08/06/2020].
Hydrogen peroxide (15 M)	0.28	Alibaba, https://www.alibaba.com/product-detail/Hydrogen-Peroxide-27-5-30-35_60480101973.html?spm=a2700.galleryofferlist.0.0.3e54287280Uohr&s=p [accessed 10/06/2020].
Li_2CO_3 (99.9 %)	15.70	Alibaba, https://www.alibaba.com/product-detail/High-purity-Li2CO3-Lithium-Carbonate_62184069940.html?spm=a2700.galleryofferlist.0.0.30ff3571Vn9p90 [accessed 10/06/2020].
Li_3PO_4 (99.9 %)	6.28	Alibaba, https://www.alibaba.com/product-detail/Lithium-Phosphate-99-9-Li3PO4-CAS_62477745804.html?spm=a2700.galleryofferlist.0.0.547f363frdxbmE [accessed 10/06/2020].
Li_2SO_4 (98 %)	19.63	Alibaba, https://www.alibaba.com/product-detail/Lithium-sulfate-10377-48-7_1319764481.html?spm=a2700.galleryofferlist.0.0.7e06cb51en1PxW [accessed 10/06/2020].
Mn_2O_3 (99.99 %)	43.18	Alibaba, https://www.alibaba.com/product-detail/High-purity-nano-Mn2O3-powder-cas_62196543133.html?spm=a2700.galleryofferlist.0.0.53e31a704lQ5WW&s=p [accessed 10/06/2020].
MnO_2 (99.9 %)	31.40	Alibaba, https://www.alibaba.com/product-detail/high-quality-MnO2-powder-manganese-dioxide_60601516322.html?spm=a2700.galleryofferlist.0.0.32fa62d8l4eVT4&s=p [accessed 10/06/2020].
$MnSO_4$ (99 %)	15.98	Alibaba, https://www.alibaba.com/product-detail/MnSo4-Manganese-Sulfate-Price_62385792090.html?spm=a2700.galleryofferlist.0.0.f3cfe15ei3rD4C&s=p [accessed 10/06/2020].
N-Methyl-2-pyrrolidone (NMP)	2.05	Echemi, https://www.echemi.com/productsInformation/pd20150901242-n-methyl-pyrrolidone.html [accessed 13/12/19]

NaCl (99.5 %)	0.79	Alibaba, https://www.alibaba.com/product-detail/Bulk-sale-sodium-chloride-anhydrous-99_60439935929.html?spm=a2700.galleryofferlist.0.0.66e17c45Y5PPk9&s=p [accessed 10/06/2020].
$NiSO_4$ (99.8 %)	43.18	Alibaba, https://www.alibaba.com/product-detail/Nickel-sulfate-hexahydrate-Nickelous-sulfate-NiSO4_62503502533.html?spm=a2700.galleryofferlist.0.0.743b2d84IbPfQc [accessed 10/06/2020].
NMC111 (98 %)	39.25	Alibaba, https://www.alibaba.com/product-detail/Li-polymer-battery-material-LiNiMnCoO2-Lithium_60761950752.html?spm=a2700.galleryofferlist.0.0.1e9d2dc3yTdXaX&s=p [accessed 10/06/2020].
Sodium hydroxide	0.47	Echemi, https://www.echemi.com/cms/7740.html [accessed 05/03/20]
Sulfuric acid (18 M)	0.21	Alibaba, https://www.alibaba.com/product-detail/97-Sulfuric-Acid-Reagent-Grade-H2SO4_60755341807.html?spm=a2700.galleryofferlist.0.0.6da269e0n6gexq&s=p [accessed 08/06/2020].

Table S4: *Calculations for total leaching cost.*

$Total\ solvent\ volume\ (L) = \dfrac{Solid\ weight\ (g)}{\frac{S}{L}ratio\ \left(\frac{g}{L}\right)}$	*1*
$Reducer\ or\ acid\ (L) = \dfrac{Reducer\ or\ acid\ concentration\ \left(\frac{mol}{L}\right) * Total\ solvent\ volume\ (L)}{Stock\ reducer\ or\ acid\ concentraton\ \left(\frac{mol}{L}\right)}$	*2*
$Reducer\ or\ acid\ price\ (£) = Reducer\ or\ acid\ volume\ (L) * Reducer\ or\ acid\ price\ \left(\frac{£}{L}\right)$	*3*
$Electrolysis\ cost\ (£) = 6.5\ kWh * \left(\frac{2}{3}\right) * Electricity\ cost\ \left(\frac{£}{kWh}\right)$	*4*
$Water\ required\ (L) = Total\ solvent\ volume\ (L) - Reducer\ volume\ (L) - Acid\ volume\ (L)$	*5*

$$Time\ to\ reach\ temperature\ (h) = \frac{\left(\frac{4182\ J\ kg^{-1}K^{-1} * solvent\ mass\ (kg) * \Delta T\ (K)}{3.6 * 10^{6}\ J\ kWh^{-1}}\right)}{Heater\ rating\ (kW)}$$	6
$$Cost\ to\ reach\ temperature\ (£) = Heater\ rating\ (W) * Time\ to\ reach\ temperature(h) * Electricity\ price\ \left(\frac{£}{Wh}\right)$$	7
$$Mass\ of\ recovered\ element\ (g) = Metal\ fraction * 1000\ kg * \left(\frac{leaching\ efficiency}{100}\right) * \left(\frac{recovery\ efficiency}{100}\right)$$	8

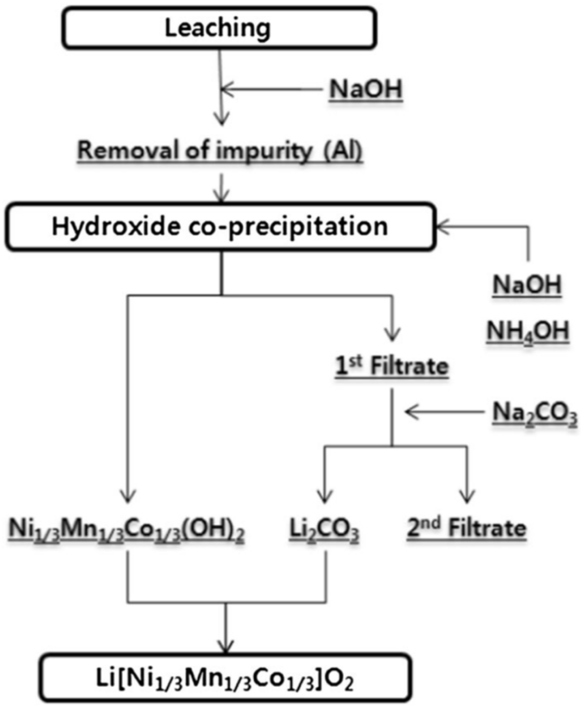

Figure 1: Flowsheet of recycling process 1.[2]

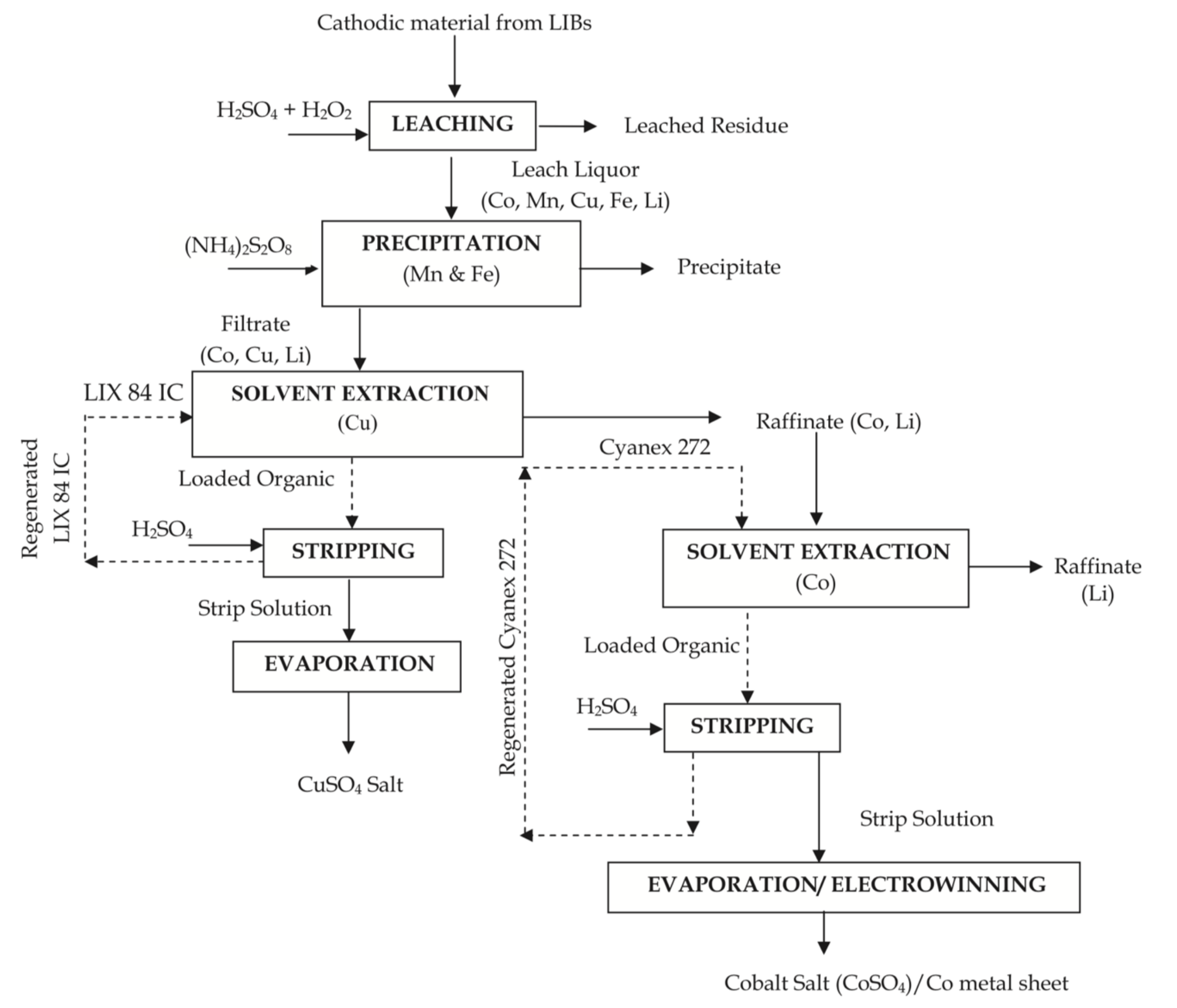

Figure 2: Flowsheet of process 2.[3]

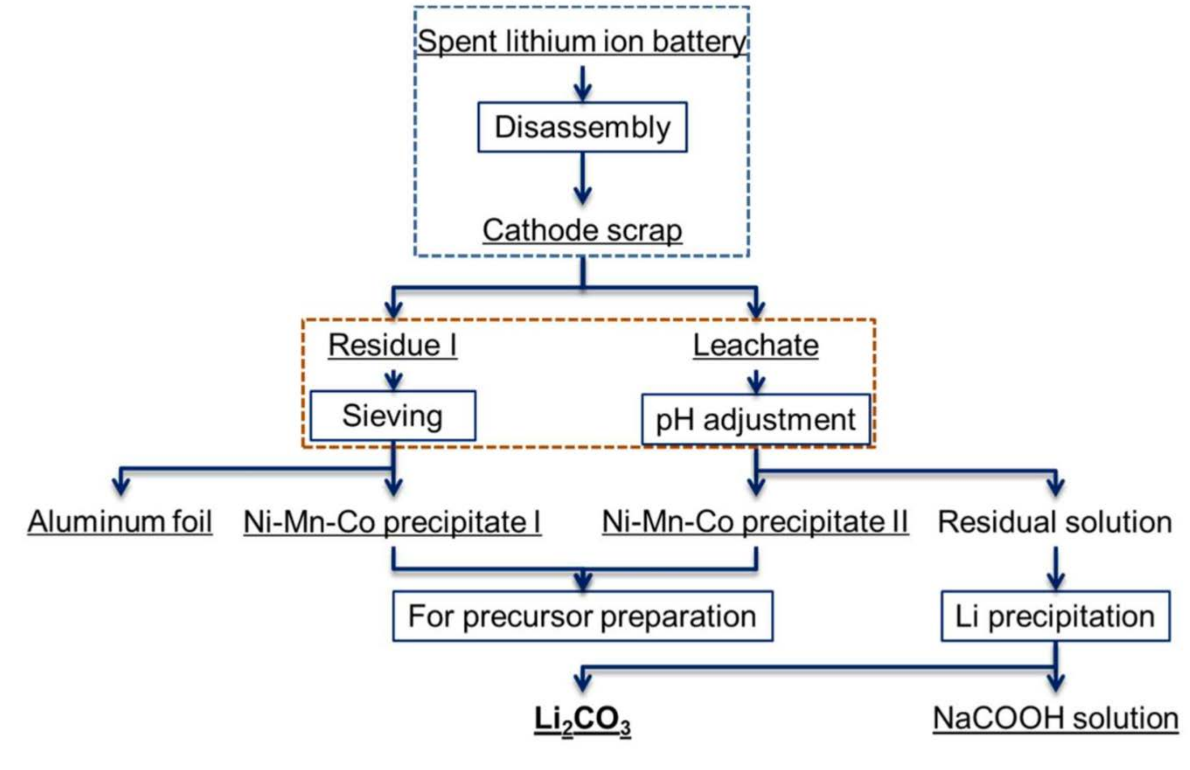

Figure 3: Flowsheet of process 3.[4]

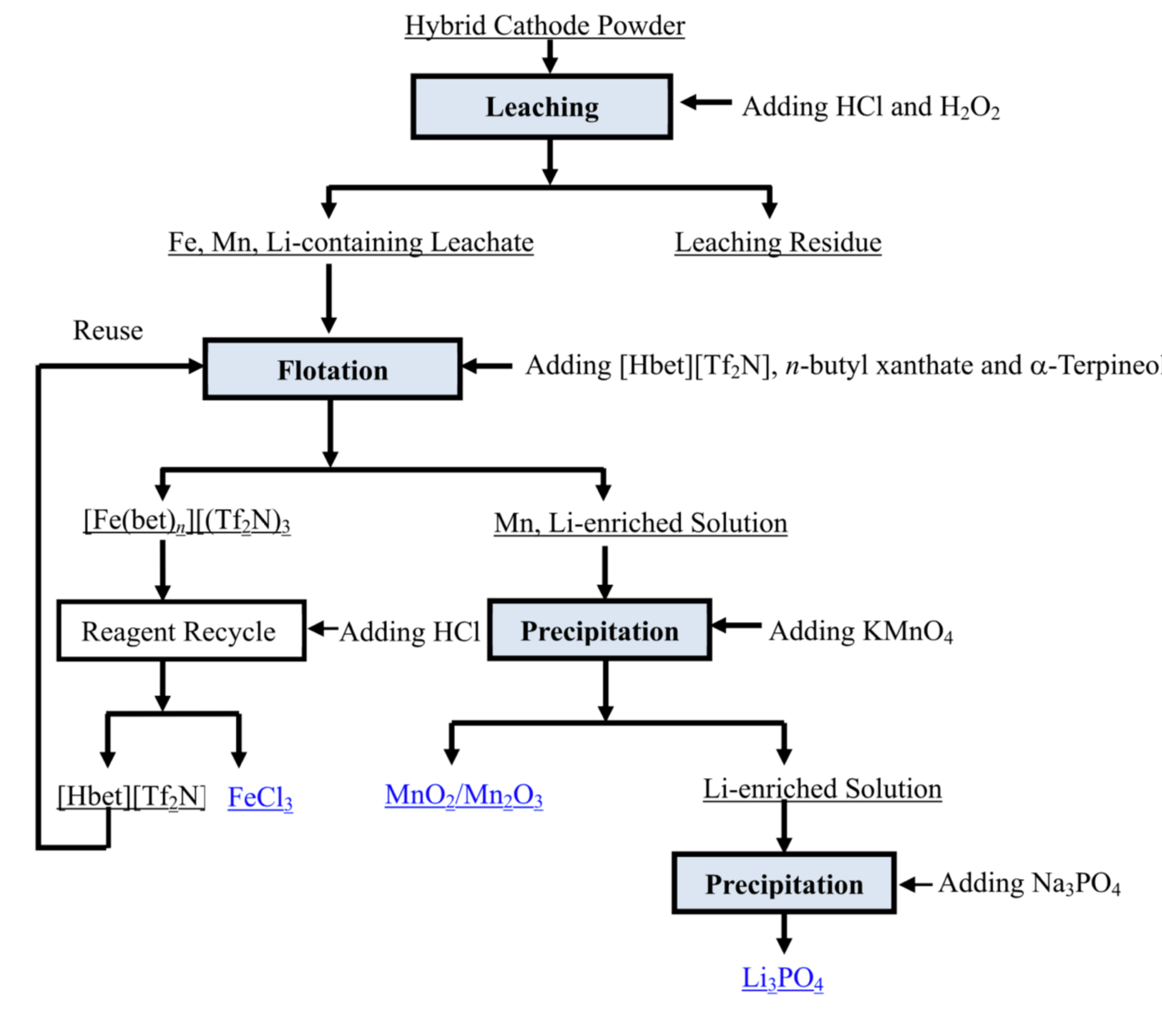

Figure 4: Flowsheet of process 4.[5]

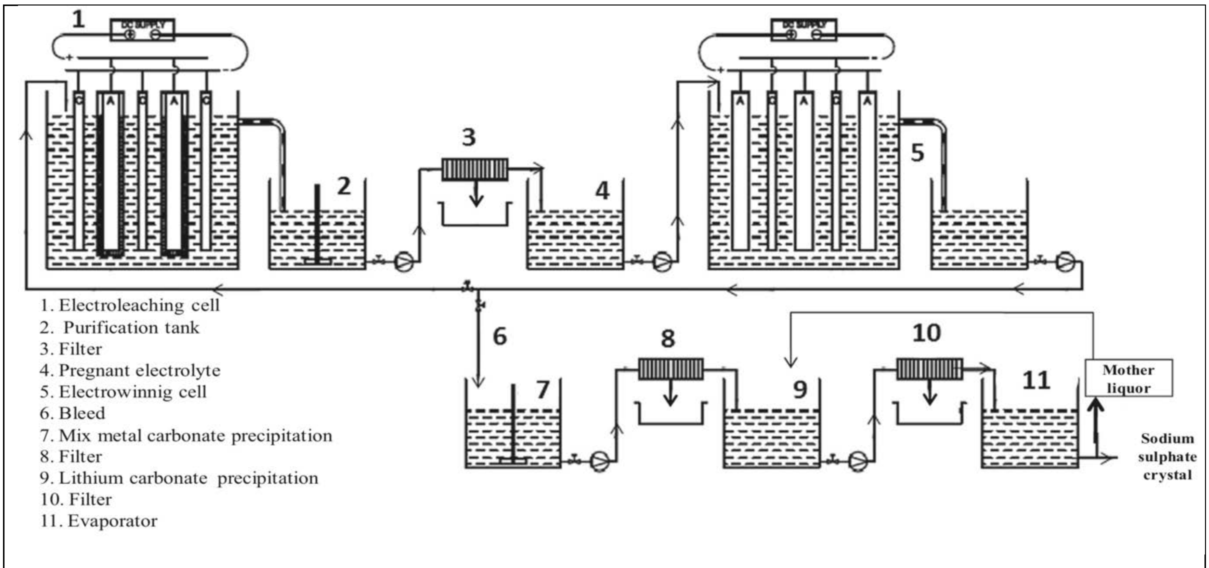

Figure 5: Flowsheet of process 5.[6]

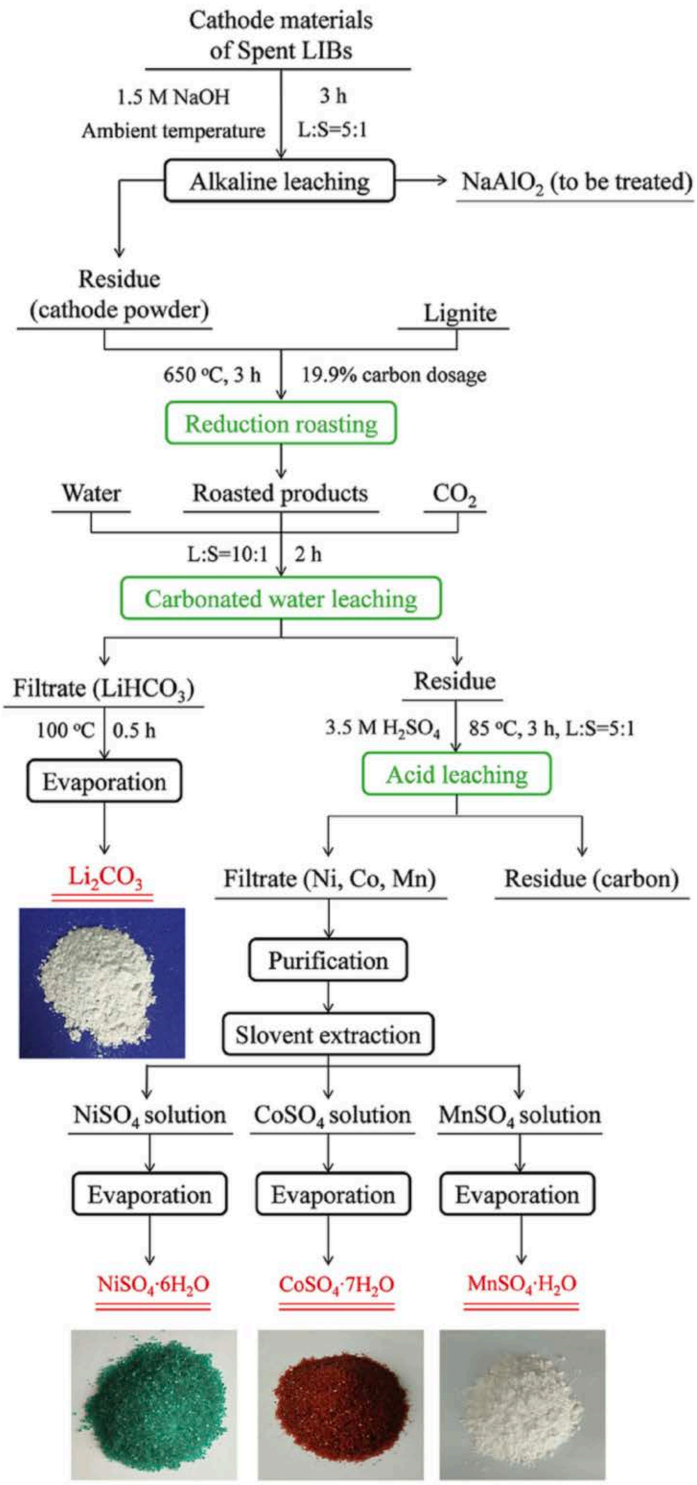

Figure 6: Flowsheet of process 6.[7]

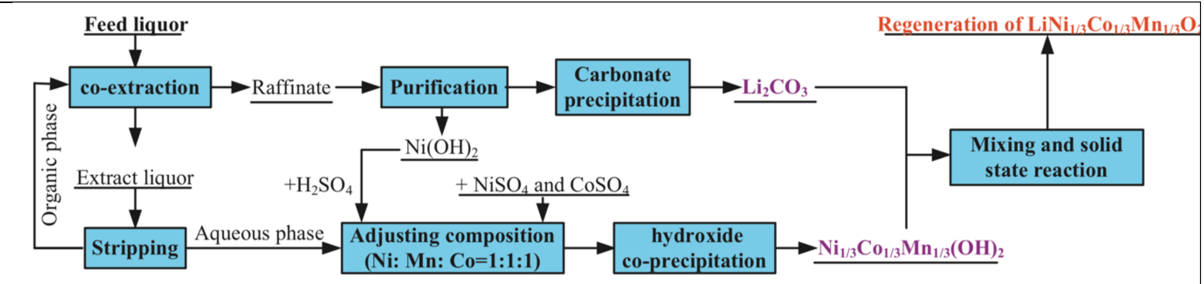

Figure 7: Flowsheet of process 7.[8]

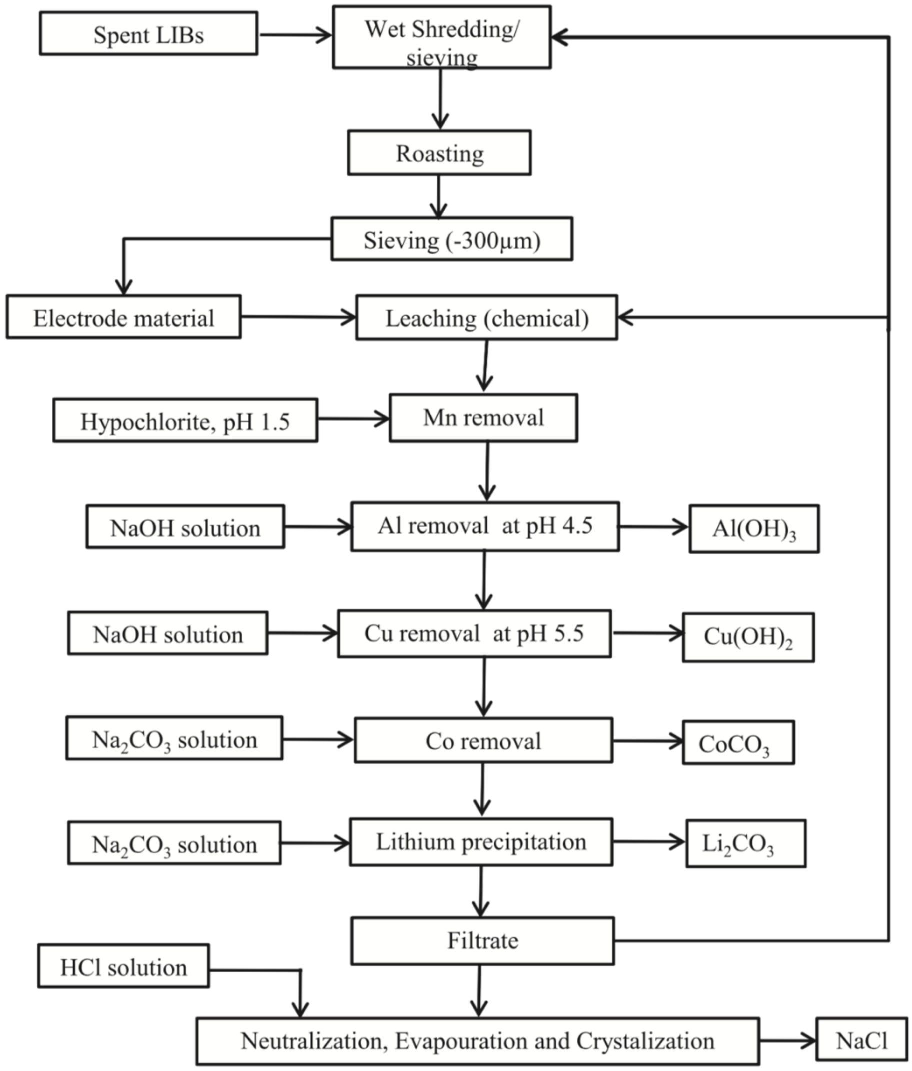

Figure 8: Flowsheet of process 8.[9]

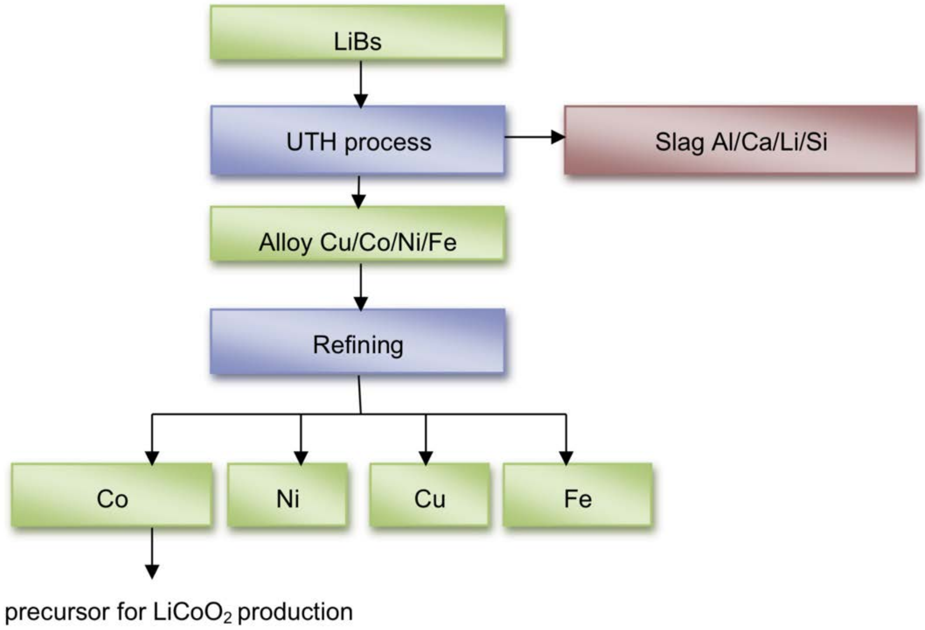

Figure 9: Umicore AG & Co. KG general recycling scheme.[10]

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