DEVELOPMENT OF AURUBIS' HYDROMETALLURGICAL LI-ION BATTERY RECYCLING PROCESS

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ABSTRACT

Aurubis AG, Europe's largest multi-metal producer and a leading Copper recycler globally, has developed and patented a hydrometallurgical process to recycle both pyrolysed and un-pyrolysed Black Mass (BM) stemming from Li-ion batteries. This purely inorganic process, comprising of leaching, precipitation, and crystallisation processes, was developed by Aurubis' R&D Hydrometallurgy Department and piloted at our Hamburg site successfully since April 2022. Aurubis' process strategy centres on a Lithium-first leach whereby a majority of Lithium is recovered as a sulphate solution which can be purified or converted into intermediates like Lithium Carbonate. Subsequently, a leach process targeting Nickel and Cobalt but including recovery of the remaining Lithium, is relatively straightforward with impurity removal following. From this leach solution, Cobalt, Manganese and Nickel are separated and recovered as intermediate products. The Graphite-rich leach residue from the Pilot plant has been used for flotation flowsheet development where concentrates of > 95% Carbon grade at 85% overall carbon recovery from locked cycle tests have already been recently presented.

We will show the evolution of the Aurubis black mass treatment process by presenting the results from consecutive pilot plant campaigns. Specifically: major value element recoveries, accountabilities and product purities achieved will be presented.

Keywords: Li-ion battery recycling, Black Mass, Critical material recycling

INTRODUCTION

The growing interest in Li-ion battery recycling over the past several years has been driven by many factors e.g., volume of battery production and associated scrap, volume of batteries expected to come to end of life and the value, rarity and criticality of the metals and materials used and finally sustainability concerns. These factors underpin European Union area legislation under Directive 2006/66/EC [1] and recently Regulation 2023/1542 [2]. Of note in the current Regulation (2023/1542);

- New batteries should contain recycled Co/Li/Ni content of 16%/6%/6%, respectively from 2031, moving to recycled Co/Li/Ni content of 26%/12%/15%, respectively from 2036.
- Collection rate of waste portable batteries from 45% to 63% to 73% starting from 2024, 2027 and 2030, respectively.
- Recycling target of 65% from 2026 for Lithium based batteries by weight, moving to 70% from 2031.
- Recycling targets for materials from waste batteries, from 2028 90% of Co/Ni/Cu and 50% Li and from 2032 95% Co/Ni/Cu and 80% Li should be reached.

Pre-processing of Li-ion battery systems is required before hydrometallurgical recovery of the active battery materials can be attempted. There exist many systems/processes to achieve this but generally, after sorting, dismantling, shredding and physical separation, Li-ion battery waste is usually well separated into copper foils, aluminium foils and a mix of Li-ion battery active anode and cathode material fractions. This active anode and cathode material produced, is known as Black Mass (BM), and is further treated to remove/recover battery electrolyte and other organic material by various methods (pyrolysis, vacuum evaporation/drying, etc;).

Aurubis AG started Li-ion battery recycling research and development in 2020. Since then, the R&D Hydrometallurgy team, based in Hamburg Germany, explored the recovery of Li-ion battery active components from BM at Lab and Pilot plant scale. The Lab development culminated in patent applications (e.g., EP4225697 B1) and consecutive Pilot campaigns have resulted in iterative flowsheet changes during which parallel lab exploration and engineering studies have had a large impact on the present flowsheet design.

PILOT PLANT HEALTH AND SAFETY

At Aurubis AG health and safety is our number one priority. BM is a hazardous material with the potential to produce HF, carcinogens, and organic components. Care was taken in the design, construction and operation of the pilot plant to make sure it was safe. The importance of the following items for Pilot Plant design, construction and operation are just as critical as for Industrial Plants.

- HAZOP Study and PLC automation of key safety systems.
- Risk assessments and Commissioning Plan.
- Hazardous gas (HF, SO_2, etc) continuous monitoring detector system.
- OHS exposure measurements and personal bio-monitoring.
- Toolbox safety talks and Work instruction review and improvement.
- Workshops to capture lessons learnt and improvements after successive Pilot campaigns.

Specific measures worth mentioning were; running all reactors under extraction through an off-gas scrubber and HF absorbent and adjusting pH to 3.5 as a minimum for fluoride containing solutions before filtration or handling. The OHS and Plant Operability learnings from the Pilot plant project have proved invaluable for the industrial scale plant design, especially considering BM is a new hazardous feed material to Aurubis.

BM PILOT PLANT FEED

Figure 1 shows the range of element variability across ~20 NMC BM samples received since 2020 at Aurubis. There is a clear variance in a) the valuable base metals Ni/Co/Cu, and b) impurities such as Al, Fe and F. Due to the relative immaturity of the battery recycling industry and the rapidly changing battery technology landscape it is very difficult to predict the future composition of a “typical” black mass. Therefore, developing a flexible process that could handle the main types of BM stemming from NCM Li-ion batteries (or even other types) was viewed as an advantage.

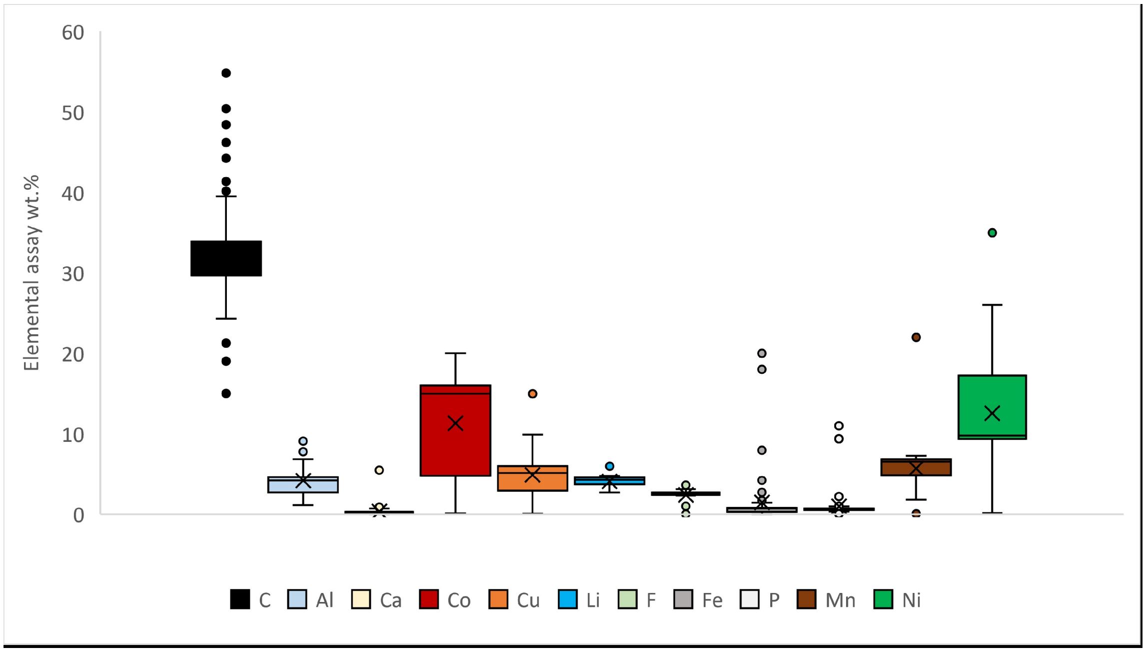

Figure 1 – Variability of Black Mass samples received from 20 suppliers showing box-whisker plots and average value (cross marker). Carbon is analysed by Hot extraction and other elements by microwave digestion-ICP-MS.

BM from two distinct pretreatment routes were elected for plant campaigns. The analytical assays for these two BM types are presented below in Table 1. The pyrolysed BM has significantly higher Co content than the unpyrolized BM. This material came from an active recycling operation and the high Co is believed to originate from Li-Cobalt-Oxide battery material more common in consumer electronics. The un-pyrolysed material seems to be of the 6:2:2 NMC cathode material origin, more common in EV applications.

Table 1 – Average elemental assay of key elements for the specific BM samples used in the Aurubis Pilot plant.

Pilot Plant BM	C	Al	Ca	Co	Cu	Li	F	P	Mn	Ni
Pyrolysed BM (Campaigns 1-3) Average wt.%	31.03	4.44	0.29	16.03	5.62	4.45	2.66	0.72	6.85	9.55
Un-pyrolysed BM (Campaign - 4) Average wt.%	48.47	1.88	0.013	3.51	1.47	3.46	2.38	0.5	4.35	15.5

PILOT PLANT STAGE 1 COMMISSIONING AND TROUBLESHOOTING

BM lab exploration started with both pyrolysed and un-pyrolysed Nickel-Cobalt-Manganese (NCM) based BM samples. Literature review informed the direction of initial test-work in the realm of oxidative and reductive acidic leaching using Sulphuric acid and various reagents. Aurubis produces of the order ~3500 t Nickel per year as a crude $NiSO_4$ crystal as an intermediate primarily from the Copper electrorefining tank house bleed solution. Therefore, the first envisaged process for BM thought to produce a similar intermediate that could be blended and sold or further refined as seen fit.

The main challenges encountered in concept flowsheet development were.

- Input material variability
    - Un-pyrolysed BM often resulted in severe foaming behaviour during leaching, especially with gaseous reagents, leading to reactor over frothing. This was believed to result from unpyrolized vacuum drying not removing all the organic binders and electrolyte constituents.

- Impurity elements
  - Copper and Aluminium are significant impurities by weight due to their role as current collector foils and they leach to some extent, requiring separation from desired end products.
  - Iron is present usually from the battery casing and components, it also leaches and requires separation from the desired end products.
  - Fluorine and Phosphorous stemming from $LiPF_6$ electrolyte constituent or similar salts used in the battery electrolyte. Fluorine is a concern when operating in acidic conditions and is not desirable in any product streams.
- Synergism with Aurubis' existing processes ($NiSO_4$ production)
  - The addition of concentrated sulphuric acid added before Ni-evaporation to promote organic species destruction and depress $NiSO_4$ solubility for a high yield producing a similar crude $NiSO_4.xH_2O$ crystal to what Aurubis already produces.
- Reagent selection
  - Oxidant reagents
  - Reductant reagents
  - Neutralising reagents

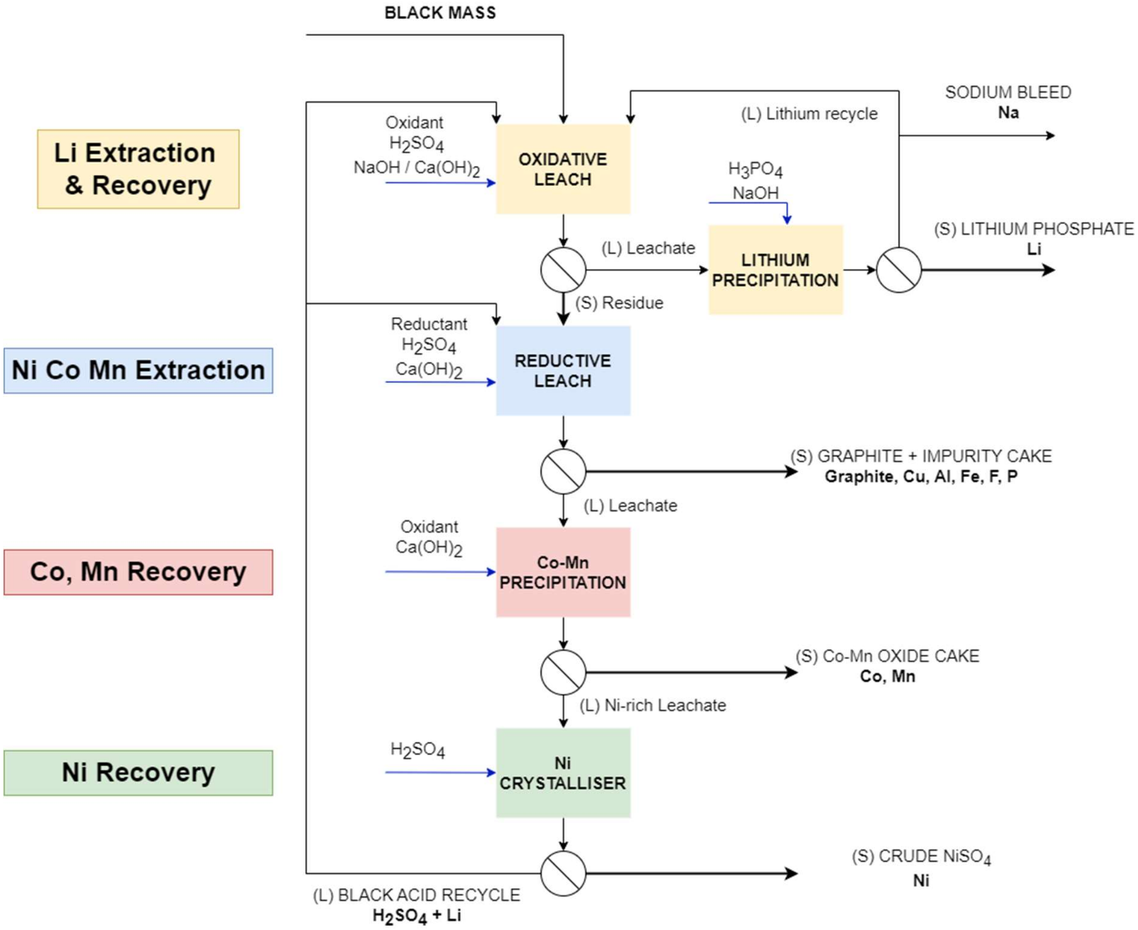

Figure 2 - Flowsheet 1, the Pilot plant was designed based on this flowsheet developed at Laboratory scale.

Figure 2 above, shows the process flowsheet that was the result of Laboratory scale development and the process that the Pilot plant was designed to emulate.

The Pilot plant consists of a mixture of stirred Glass and Metal reactors of 50 – 200 L volume with Filtration equipment (0.1 m^2 to 0.22 m^2 Pressure filters, Vacuum filtration).

Figure 3 – Photograph of the Pilot plant showing Reductive leach system and Lithium evaporation system.

The first oxidative leaching step was performed at mildly acidic conditions with a strong oxidising agent to promote de-lithiation of the Cathode-active-material (CAM) Ni-Mn-Co-oxide structure rather than the complete dissolution of that structure. In this way Li was leached to a sulphate solution, which after neutralisation was practically free of other metals. Filter cake wash water was recycled to provide initial suspension water.

The Li solution was then forwarded to an evaporation/precipitation step. The Li-phosphate product was selected due to its low solubility and high potential yield. Phosphoric acid was added with continuous sodium hydroxide addition to maintain alkaline conditions. The filtrate from this step was recycled to the first leaching process to recover the low residual concentration Li with a bleed for Na concentration control.

The residue from the first oxidative leach was re-suspended and forwarded to the reductive leaching step which is more strongly acidic and uses reducing conditions to fully dissolve any remaining metal-oxide structure allowing almost complete recovery of Ni/Co/Mn and remaining Li to solution. Lime was added at the end of this process to partially precipitate impurities (e.g., Al/Cu/Fe/F) and importantly shift pH out of the HF activity zone. Filter cake wash water from this stage was used as re-pulping water for the residue coming from oxidative leaching.

The leachate from the reductive leach process was then re-processed with oxidant to selectively precipitate Co and Mn from solution and therefore produce a Ni-rich sulphate solution. This Ni-leachate was acidified and evaporated to produce the $NiSO_4.xH_2O$ crystal product and the concentrated “Black acid” leftover after filtering the crystals was used to substitute fresh sulphuric acid in the upstream processes and ultimately recovers the contained Li (~10% of Li is recovered via this manner).

Two Pilot campaigns operated with Flowsheet 1 configuration with the aims listed below. Campaign 1 encountered several equipment breakdown issues and was used for plant commissioning and confirming if optimised conditions from the Lab test work did also hold at Pilot scale. Campaign 2 was a lock-cycle campaign where the main aim was to achieve Black acid recycle and study how impurities built up in each area with consistent recycling of wash waters.

Campaign 1 – Commissioning and Optimisation

- Equipment commissioning through all process steps.
- Developing operating instructions and protocols.
- Temperature, pH and batch duration optimisation confirmation for leaching and precipitation processes.

Campaign 2 – Flowsheet 1 Lock-cycle attempt

- Metal recovery and distributions to close the Mass Balance and underpin a Process model and Process Design Criteria for Engineering Cost Studies.
- Study how and where impurities build up with Cake wash water and $NiSO_4$ mother liquor recycle streams.
- Measure steady state reagent consumptions for OPEX estimation.
- Produce kg scale product samples and assay product quality for commercial considerations.

Product Quality – Campaign 2

Table 2 shows the Li-phosphate produced contained significant amounts of sodium and fluorine. These are present due to the evaporation stage to increase Li concentration prior to precipitation. The evaporation together with NaOH addition formed Na_2SO_4 at saturation. These impurities should be avoidable with further product washing and re-filtration. The fluorine impurities were assumed to be a LiF precipitate formed during evaporation.

Table 2 - Lithium Phosphate product quality from Pilot Campaign 2.

Li_3PO_4	Li	P	Al	Co	Cu	F	Fe	Mn	Na	Ni
Average (%)	17.6	19.7	0.09	0.01	0.01	2.98	0.01	0.00	2.59	0.01
Min. (%)	15.0	17.0	0.005	0.001	0.001	0.78	0.001	0.001	0.001	0.001
Max. (%)	21.0	22.0	0.23	0.024	0.01	6.3	0.045	0.0062	6.3	0.013

The advantage of Li-phosphate production is a very low solubility limit (~0.3 g/L Li) which enables a very high yield from less concentrated Li-filtrate, for example compared to Li-carbonate (~3-4 g/L Li solubility limit). The disadvantages of this were the high cost of Phosphoric acid and the need for addition Caustic soda as neutralising agent adding to the Na-load of the circuit.

Table 3 Co-Mn Oxide Filter Cake product quality from Pilot Campaign 2.

Co-Mn Cake	Co	Mn	Al	Ca	Cu	F	Fe	Li	Ni	P	H_2O
Average (%)	13.06	7.76	0.51	14.43	1.87	0.34	0.49	0.02	0.84	0.03	56.9
Min. (%)	3.60	3.80	0.18	10.00	0.42	0.05	0.05	0.01	0.26	0.01	46.1
Max. (%)	19.00	23.00	1.20	16.00	3.00	0.56	3.10	0.13	2.10	0.15	62.0

The Co-Mn precipitation filter cake contains a high proportion of Gypsum due to Lime addition during the reaction to control pH (as the Co/Mn oxidation reaction produces acid). A portion of Al, Cu, Fe and Ni reported to this Filter cake. Fe likely precipitated as Ferric sulphate due to the oxidative conditions, but Al/Cu/Ni should have remained in solution at this process pH and could have been present due to poor Filter cake washing or localised precipitation due to Lime suspension dosage and mixing conditions. It is undesirable to lose any Ni to this product, however a high recovery of Co and Mn and separation from the remaining Ni filtrate was achieved, which should have effectively removed Co and Mn from the Nickel product.

Table 4 - Acidic NiSO4.xH2O crystal product quality from Pilot Campaign 2.

$NiSO_4.xH_2O$	Ni	Al	Ca	Co	Cu	F	Fe	H_2SO_4	Li	Mn	P
Average (%)	15.79	0.1	1.68	1.25	3.93	0.09	0.09	19.74	0.18	0.18	0.01
Min. (%)	7.10	0.05	0.03	0.14	1.10	0.01	0.02	12.00	0.04	0.03	0.01
Max. (%)	20.30	0.3	4.40	3.10	5.90	0.30	0.28	31.30	0.29	0.26	0.01

Aurubis currently produces an acidic $NiSO_4$ intermediate with ~23 wt.% Nickel and ~15 wt.% H_2SO_4 content. However, producing this type of $NiSO_4$ crystal from BM comes with some additional concerns, with Fluorine being concentrated during evaporation at highly acidic conditions. This means both personal safety concerns due to HF risk and materials of construction are both troublesome. The impurity profile is also very high, with especially Cu crystallising out at this step, not being removed in previous process steps.

Recoveries – Campaign 2

Unfortunately, overall Campaign 2 mass accountability was < ≈70% due to several factors. Therefore, overall recoveries were calculated using HSC Sim modelling, with the stage-by-stage elemental distribution from the Pilot plant results. Individual process step accountability was generally > 90%, however the overall mass accountability for the whole Pilot campaign was not acceptable to the R&D team. Improving mass balance accountability was a major focus of the following campaigns described below.

From the HSC Sim modelling, > 95% recoveries of Li, Co and Mn to their main products were calculated. However, Ni recovery to $NiSO_4$ product was < 90%, with significant losses in the reductive leaching stage (attributed to poor leaching efficiency, filtration and washing), Co-Mn filter cake (attributed to $Ca(OH)_2$ mixing, filtration and washing) meaning recovery was only calculated to be 82%.

Table 5 – Pilot Campaign 2 overall elemental recovery to output streams.

Distributes To	**Al**	**Co**	**Cu**	**Li**	**Mn**	**Ni**	**F**
	%	**%**	**%**	**%**	**%**	**%**	**%**
Li-Phosphate/Li-Filtrate	0	0	0	<u>96</u>	0	0	47
Graphite-Impurity Cake	<u>78</u>	3	<u>17</u>	1	3	7	<u>27</u>
Co-Mn Oxide Cake	21	<u>96</u>	61	1	<u>96</u>	11	26
Ni-Sulphate	1	1	22	2	1	<u>82</u>	< 1
Overall Mass Accountability	75	67	59	66	70	60	57

PILOT PLANT STAGE 2 . FLOWSHEET EVOLUTION AND FOCUS ON ACCOUNTABILITY

Issues Discovered from Campaign 1 and 2

1. Nickel recovery < 90%.
2. H_3PO_4 cost to produce Li_3PO_4 product.
3. High amount of NaOH addition leading to Na in Li-product and requiring Na-removal or large bleed stream. Cost of NaOH.
4. Fluorine deportment to products, especially to the Lithium stream.
5. Acidic $NiSO_4$ purity and Fluorine levels in acidic crystalliser liquid/mother liquid.
6. < ≈70% overall accountability due to Pilot plant operation and mass loss meaning a poor level of confidence for mass balancing and PDC.

Solutions

1. Improve Filtration and Cake washing in Reductive leach and Co-Mn Precipitation while improving $Ca(OH)_2$ addition to minimise unwanted localised precipitation.
2. Change to a Li-carbonate product to remove Phosphoric acid from the process.
3. Substitute a portion of NaOH with $Ca(OH)_2$ during neutralisation of oxidative leach liquor to prevent F deportment to the lithium stream.
4. Quantitatively remove Na from the system as Glauber salts and produce Anhydrous Na_2SO_4 as a by-product.
5. Change to conventional $NiSO_4.6H_2O$ Crystallisation with pre-evaporation to concentrate impurities before a specific Impurity removal step with Lime before final $NiSO_4$ crystallisation stage.
6. No $NiSO_4$ acidification, i.e., no black acid production, Ni-mother liquor recycled completely to Oxidative leaching step for Li recovery.
7. Target > 90% mass accountability for next campaign
    a. Process steps were collected under an overall Pilot Plant batch integrity concept.
    b. All wastewater, sump water and solids reporting to the sump were collected, mass or volume recorded and assayed.
    c. Sampling plan focussed entirely on elemental mass accounting for each batch and kinetic samples were not taken.
    d. Start empty and finish empty philosophy, with a planned flush out and clean out of each reactor system was performed after their final batch, end Wash waters were forwarded to next process step for processing, all culminating in filtering the sump contents.

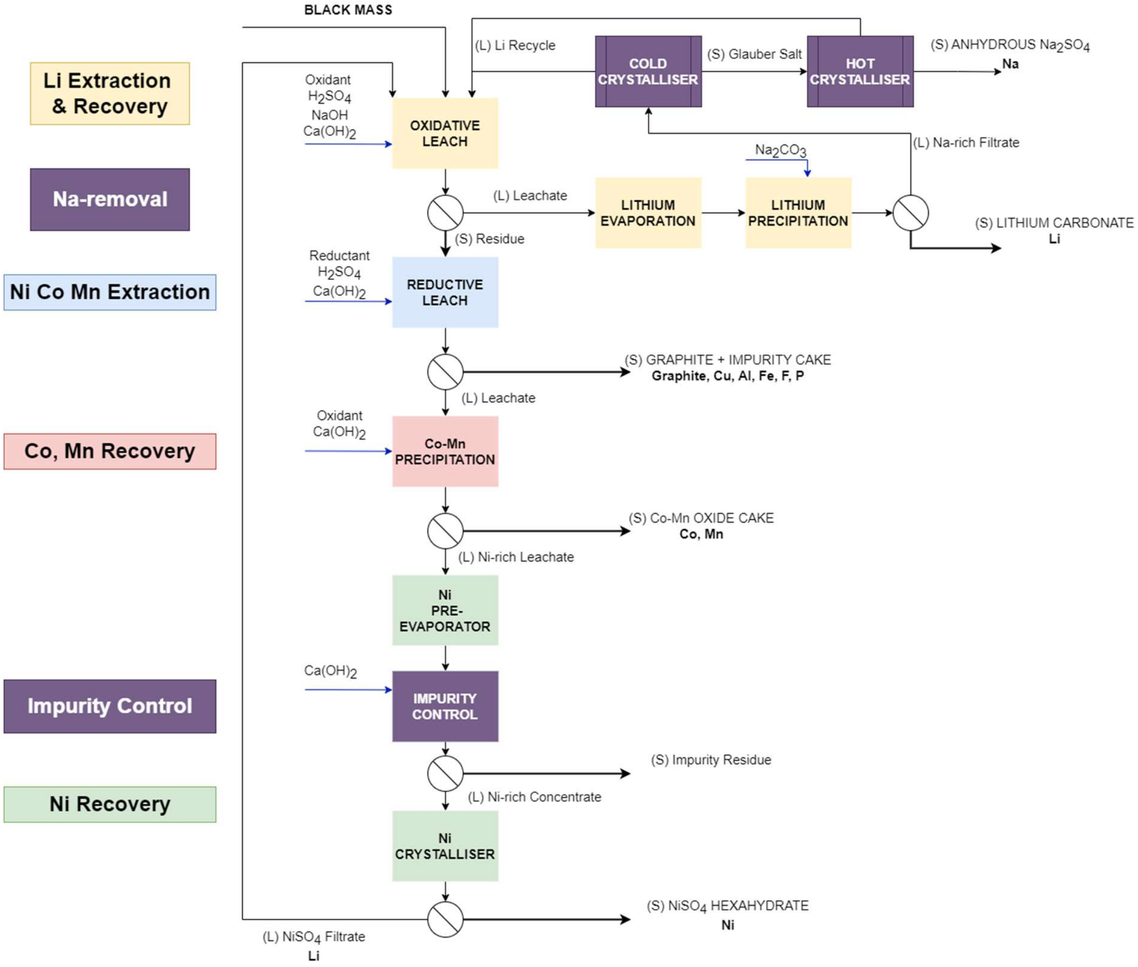

Figure 4 - Flowsheet 2, Campaign 3 flowsheet was updated to solve the problems encountered after Piloting the first flow sheet

The Stage 2 flowsheet shows the changes made after reviewing the problems encountered in Campaign 1 and 2 (Figure 4 above). The Pilot plant was adapted to suit these added process steps with new reactors installed for Li_2CO_3, Na_2SO_4, Impurity removal and $NiSO_4$ crystallisation steps. The original Li precipitation reactor was still used for evaporation so as to concentrate the Li filtrate to > 20 g/L [Li] for better yield of Li-carbonate and the original Ni evaporator was used for the bulk pre-evaporation before the smaller volume being transferred to Impurity removal and final crystallisation.

Product Quality – Campaign 3

Li-carbonate produced was a significant improvement in terms of impurities when compared to the earlier Li-phosphate product. Partial $Ca(OH)_2$ addition during Oxidative leach neutralisation stage was found to precipitate fluorine to < 100 ppm in Neutral leach filtrate. Therefore, fluorine levels in the Li product were much lower.

Table 6 – Lithium Carbonate product quality from Campaign 3

Li_2CO_3	Li	C	Al	Ca	Co	Cu	F	Fe	Mn	Na	Ni
Average (%)	18.64	16.12	0.002	0.14	0.02	0.001	0.165	<0.01	0.002	0.322	0.003
Min. (%)	18.52	16.02	0.000	0.01	0.00	0.000	0.080	<0.01	0.000	0.240	0.000
Max. (%)	18.71	16.18	0.003	0.3	0.05	0.002	0.320	<0.01	0.005	0.560	0.007

Pre-evaporation of the Li filtrate up to the point of Li sulphate solubility allows for a large portion of Calcium to be removed as insoluble $CaSO_4$ and CaF_2 before carbonate precipitation. Li-carbonate precipitation with saturated Na_2CO_3 solution did result in some Na_2SO_4 salting out into the Li-carbonate product but this was effectively washed out of the Li_2CO_3 cake with hot water and could be further improved by additional washing steps. Further purification by pre-treatment to remove di-valent cations and Fluorine would result in a technical grade Li-carbonate.

Table 7 below shows that Campaign 3 Co-Mn oxide filter cake was relatively similar to Campaign 2, considering no changes were made to the Reductive leach or Co-Mn precipitation stages.

Table 7- Co-Mn Oxide Filter Cake product quality from Pilot Campaign 3

Co-Mn Cake	Co	Mn	Al	Ca	Cu	F	Fe	Li	Ni	P	H_2O
Average (%)	12.77	5.86	0.66	14.50	2.33	0.49	0.42	0.01	0.84	0.02	51.83
Min. (%)	12.00	5.00	0.06	13.00	0.38	0.36	0.28	0.00	0.26	0.01	43.90
Max. (%)	13.00	6.50	0.84	15.00	3.60	0.60	0.49	0.03	2.10	0.04	58.37

The Nickel sulphate hexahydrate crystal product produced was acid-free and also with significantly lower amounts of impurities (Al, Cu, F, Mn, Co). Therefore, much more suitable to further refining than the acidic $NiSO_4$ produced in Campaign 2. Sodium impurities were still present due to the relatively minor amounts of Na making its way via the Oxidative leach residue cake into the rest of the process.

Table 8 – Acid-free Nickel Sulphate hexahydrate crystal product produced from Pilot Campaign 3

$NiSO_4.6H_2O$	Ni	Al	Ca	Co	Cu	F	Fe	Na	Li	Mn	P
Average (%)	16.26	0.011	0.18	0.25	0.25	0.05	<0.01	2.61	0.32	0.033	0.10
Min. (%)	14.69	0.002	0.11	0.14	0.05	0.005	<0.01	1.14	0.24	0.006	0.07
Max. (%)	16.95	0.03	0.23	0.98	0.59	0.09	<0.01	4.87	0.38	0.085	0.14

Recoveries – Campaign 3

Campaign 3 recoveries were calculated from measured masses, volumes, densities and elemental assays performed by the Aurubis Analytical Lab in Hamburg. For Li, Co and Mn the overall recovery to products was comparable to Campaign 2 at > 95%, with Ni being the major change dropping to 73% recovery to $NiSO_4$ product. Ni losses to Graphite cake and Co-Mn product were marginally lower due to filtration and washing improvements, however, the Impurity control process-step resulted in significant Ni recovery losses (although being an effective quantitative removal of Fluorine plus other impurities). The overall mass accountability of Campaign 3 was good with total mass, water and most value elements being accounted for at > 90%. Fluorine accountability remained a problem indicating a potential issue with analysis or unmeasured losses (e.g., Off-gas). Campaign 3 achieved the main goal of producing a result with a sufficient level of confidence to generate a mass balance and process design criteria to underpin a feasibility study.

Table 9 - Pilot Campaign 3 overall elemental recovery to output streams.

Distributes To	Al %	Co %	Cu %	Li %	Mn %	Ni %	F %
Li-Carbonate	0	0	0	95	0	0	<1
Graphite-impurity cake	71	2	24	2	2	5	36
Co-Mn Oxide Cake	17	97	35	< 1	97	10	26
Impurity removal cake	12	< 1	20	2	< 1	12	38
Ni-Sulphate	0	1	21	1	1	73	<1
Mass Accountability	92	90.8	98	98.5	91.6	93.7	70

PILOT PLANT STAGE 3 - UNPYROLZED BLACK MASS AND FURTHER FLOWSHEET EVOLUTION

Issues discovered in Campaign 3

- Na-removal from the process resulted in voluminous amounts of Glauber salts and scaling this process up is not trivial in terms of CAPEX/OPEX and sale of ensuing volumes of anhydrous Na_2SO_4 (which must be of a high purity).
- Li-carbonate production was straightforward and produced a higher-quality product but still required Na-input like the Li-phosphate product.
- Specific Impurity control step was successful in removing impurities before Ni-crystallisation but resulted in significant Ni losses.
- The Co-Mn oxide product has a high impurity profile and therefore complicates further Co refining.

Solutions

- Full substitution of NaOH with $Ca(OH)_2$ in the Oxidative leach neutralisation step. This has a downside, increasing the solid reside and consequently the sizing and cost associated with solid-liquid separation step. However, usage of Lime at this stage is important for impurity rejection from the Lithium product stream.
- Produce a Li sulphate concentrate solution or $Li_2SO_4.H_2O$ crystal product to have a Na-free circuit.
- Impurity control precipitation moved upstream of Co-Mn precipitation to reject impurities from the Co and Ni products. Recycling of Impurity residue back to Reductive leach to recover entrained Ni/Co and force impurities out via the Graphite residue.
- Develop further treatment of Co-Mn Oxide product to produce a $CoSO_4$ intermediate and Mn-residue separately.

Extensions

- Un-pyrolysed BM feed material was used and its impact on the process, recoveries and product quality could be studied.
- Included Graphite recovery process via Flotation in process flowsheet and continued sending Reductive leach residue for flotation amenability and flowsheet test-work.

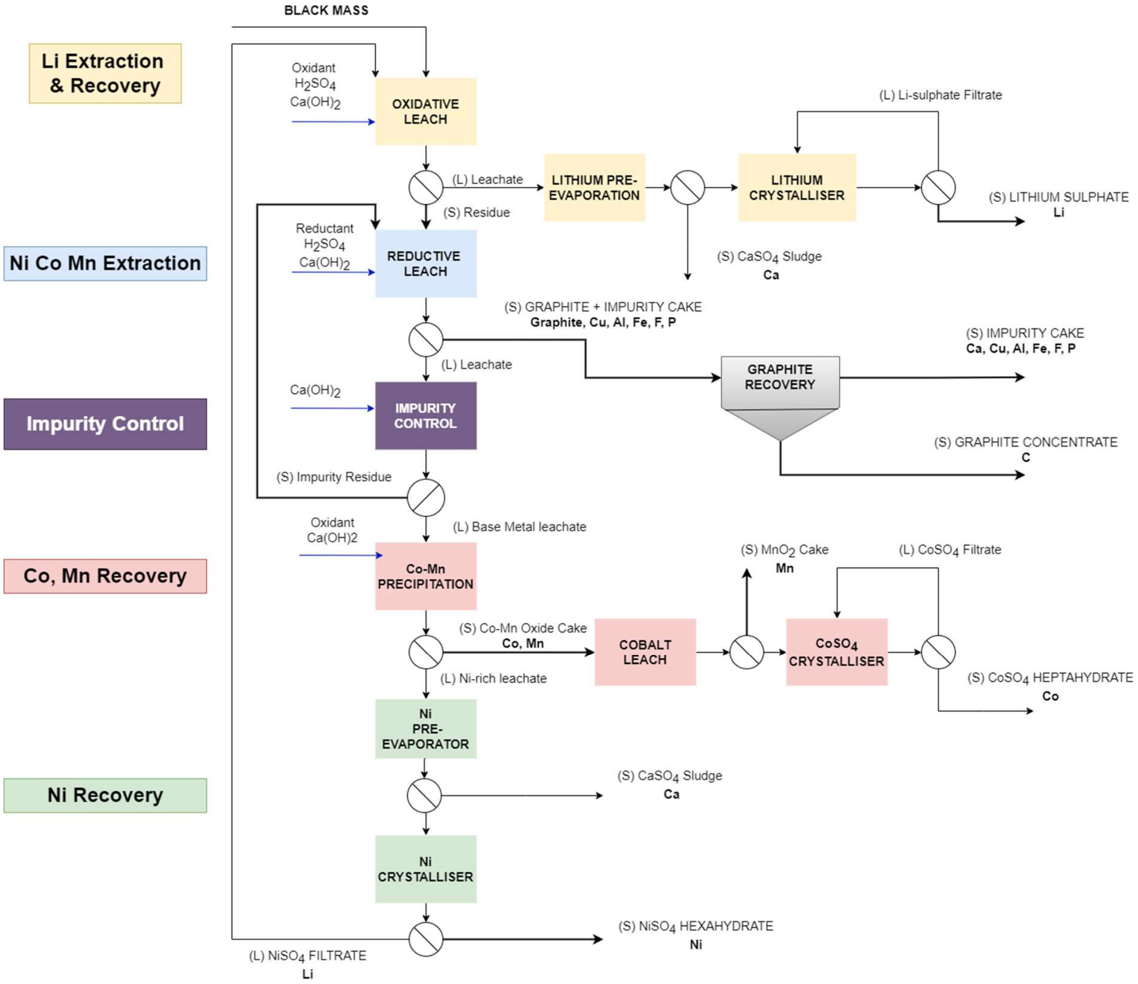

Figure 5 - Flowsheet 3, Pilot Campaign 4 was updated to address problems discovered in Campaign 3 while Graphite and $CoSO_4$ production are now included in the holistic view.

Figure 5 shows the evolution of the flowsheet to its present form. In the core process there was no longer a need for Na-removal and the Impurity control step was moved before Co-Mn Precipitation to improve product quality. Graphite recovery from the Reductive leach residue has been presented recently and consists of conventional flotation process producing a >95 % Carbon grade concentrate with ~85% carbon recovery [3]. Co was re-dissolved from the Co-Mn precipitate cake selectively over Mn and the resulting Co-rich sulphate liquor was evaporated and crystallised to form a $CoSO_4.7H_2O$ crystal.

Product Quality – Campaign 4

Both the Li sulphate solutions and the single batch of crystals produced from Campaign 4 still had very low F content with the benefit of virtually eliminating sodium. Calcium and Fluorine could potentially be further reduced with ion exchange treatment if required. Pre-neutralisation with only lime had the benefit of eliminating most of the F and base metals from the Li stream while negating the need to introduce sodium to the stream.

Table 10 – Lithium sulphate products from Campaign 4, 2 batches of concentrated Lithium solution were produced and a single batch of Lithium sulphate monohydrate crystals were produced.

Li_2SO_4 Concentrate	Li	Al	Ca	Co	Cu	F	Mg	Mn	Na	P
Batch 1 g/L	25	< 0.01	0.37	<0.01	<0.01	0.1	0.02	<0.01	1.3	2.4
Batch 2 g/L	31	< 0.01	0.37	< 0.01	< 0.01	<0.1	0.04	< 0.01	0.54	2.9
$Li_2SO_4.H_2O$ Crystals	Li	Al	Ca	Co	Cu	F	Mg	Mn	Na	P
Single batch wt.%	10.65	<0.005	0.103	<0.005	<0.005	0.76	<0.005	<0.005	0.076	0.18

The main differences in the Co-Mn Oxide cake produced from this stage is explained in terms of the difference in feed BM to Campaign 1 - 3 versus Campaign 4. The pyrolysed BM for campaigns 1-3 had much high Co and lower Ni than the unpyrolized BM and as such the Co-Mn oxide filter cake had lower levels of Co and relatively higher content of Ni most probably due to insufficient wash out the high Ni containing filtrate from campaign 4. The lower Al, Cu and Fe values reflect the impurity removal step included before this stage (Figure 5).

Table 11 - Co-Mn Oxide cake produced from Campaign 4

Co-Mn Cake	Co	Mn	Al	Ca	Cu	F	Fe	Li	Ni	P	H_2O
Average (%)	9.08	5.86	0.13	15.62	0.645	0.30	0.02	0.01	2.68	0.02	55.98
Min. (%)	7.75	5.00	0.018	15.0	0.17	1.1	0.01	< 0.01	2.05	0.01	44.91
Max. (%)	9.95	6.50	0.52	17.0	2.2	0.1	0.03	0.03	4.15	0.04	66.40

The selective leach of Co from the Co-Mn Oxide cake yielded good results in terms of separating the Co from the Mn improving it for further refining. The next opportunity for optimisation would be the removal of Ni (and also Cu) which would also represent a recovery opportunity for Ni in the overall flowsheet.

Table 12 – Cobalt sulphate crystal product produced at laboratory scale from Pilot plant Co-Mn oxide cake from Campaign 4.

$CoSO_4.7H_2O$	Co	Al	Ca	Ni	Cu	F	Fe	Na	Li	Mn
Single batch wt.%	13.96	0.08	0.1	4.67	1.38	0.01	< 0.01	< 0.01	0.005	< 0.01

The Ni-sulphate hexahydrate produced during Campaign 4 had a substantially higher Ni content that Campaign 3 mainly due to the reduction in sodium. The impurity removal stage relocated to before the CoMn precipitation stage still yielded the same benefits in terms of Cu, Al, Fe and F reduction in the final crystal. Reduced levels of Co and Mn as compared to Campaign 3 resulting from improved operation of the Co-Mn precipitation stage also contributed to the crystal quality.

Table 13 – Nickel sulphate hexahydrate crystal product produced from Campaign 4

$NiSO_4.6H_2O$	Ni	Al	Ca	Co	Cu	F	Fe	Na	Li	Mn
Single batch wt.%	21.84	0.009	0.41	0.084	0.014	0.078	0	0	0.26	0.017

Graphite Flotation Extension

Table 14 below highlights the quality of Graphite obtainable by conventional flotation of the main Aurubis Hydromet process residue. The Graphite concentrate was produced by lock-cycle flotation flowsheet testing from Campaign 3 Graphite-Impurity Filter cake.

Table 14 – Graphite concentrate produced from lock-cycle flotation test-work using Campaign 3 reductive leach residue as feed material.

Flotation Concentrate	C	Al	Ca	Ni	Cu	Fe	Li	Mn
Washed Lock Cycle Con. wt.%	96.7	1.35	0.48	0.093	0.18	0.175	0.02	0.01

Recoveries – Campaign 4

Table 15 shows that accountabilities > ≈90% were achieved in Campaign 4 with a few exceptions. The Cu accountability of 130% is assumed to be a result sampling inconsistency of Cu content in BM feed material. Cu is usually present in larger particle size distribution and despite sieving and attempted representative sampling it is probable that there was large size Cu segregation in sample containers. Fluorine accountability remains consistently < 70% in all campaigns and more effort will be devoted to analytical techniques for solids and liquids and checking effluents from all parts of the pilot plant. From a recovery perspective, a significant improvement in Ni recovery was made when compared to previous campaigns. This was mostly driven by improved leaching of Ni in the Reductive leach stage but also by successful recycling of the Fluorine-Impurity filter cake. However, Ni distribution to the Co-Mn Oxide cake or $CoSO_4$ product is a clear opportunity for improving Ni recovery to $NiSO_4$ product and should be investigated.

Table 15 - Pilot Campaign 4 overall elemental recovery to output streams.

Distributes To	Al %	Co %	Cu %	Li %	Mn %	Ni %	F %
Li-Sulphate	< 1	< 1	< 1	96	< 1	< 1	1
Graphite-Impurity Cake	95	2	84	1	2	1	91
Co-Mn Oxide Cake	3	96	13	<1	97	7	4
Ni-Sulphate	2	2	3	3	1	92	4
Mass Accountability	101	107	130	95	91.6	99	64

CONCLUSIONS AND FUTURE DIRECTION

In this paper the evolution of the Aurubis BM recycling process has been discussed following the progress made through 4 piloting campaigns. There is a vast amount of open domain literature focused on individual unit operations, mostly leaching, required to treat or recycle Li-Ion BM. However, a fully integrated flowsheet is required to do this commercially and there is a paucity of information available in the open domain regarding this. Particularly lacking is process descriptions, impurity management and deportment, value element recovery and product or intermediate product quality, reagents utilised, and byproducts produced. Most presentations or publications of pilot plant operations typically only present overall claimed recoveries of value elements with very little information on the pilot plant campaign accountability which provides the reader with very little insight into the level of confidence one can expect in these results.

So far, Aurubis R&D has focussed on developing a robust process to maximise recovery of all valuable components as intermediates as opposed to battery grade products. For example, contrary to many Battery recycling processes, Aurubis has developed Graphite recovery, which is undervalued by the industry (particularly Pyrometallurgical processes), as it represents a large mass of Li-ion batteries and is not foreseen to be replaced as the main anode-material [4].

The process which has been piloted several times with a high level of confidence, has evolved into a robust process with the following distinguishing attributes:

- Processing pyrolysed and un-pyrolysed BM feed types
- Solvent extraction free core separation process
- Li-first recovery
- Graphite recovery
- Sodium free process

The process is continuously being developed along with demo plant scale equipment being commissioned this year for certain unit operations.

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