EnAM BASED ON LITHIUM-ION-BATTERIES PYROMETALLURGICAL TREATMENT

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Introduction

Recycling lithium-ion batteries (LIBs) typically involves mechanical separation of metals, thermolysis to break down organics, and pyrometallurgical or hydrometallurgical steps[1,2]. Pyrometallurgical treatments are robust for recovering valuable metals from End-of-Life (EoL) LIBs, allowing direct processing with minimal or no previous treatment, yielding an alloy rich in Co, Ni, Cu, Fe, and Mn and a lithium-rich slag[1]. Traditional processes, such as the Umicore method, primarily reduce metals like copper, cobalt, and nickel to alloys while leaving lithium in the slag[3]. Treatment includes using slag formers such as CaO, Al_2O_3, and SiO_2 to control melting point and viscosity.

Efficient lithium extraction from this Li-containing slag has become crucial for improving recycling pathways. Some authors demonstrated that nearly 100% lithium leaching efficiency could be achieved at 80 °C from lithium slag containing $LiAlSiO_4$ and Li_2SiO_3 phases[1]. However, direct leaching produces silica gel that complicates filtration and further extraction[3]. Lithium recovery after pyrometallurgical treatment becomes difficult when the slag is in a silica-rich or amorphous structure. The German Project LiBRi[4] demonstrated that lithium aluminates ($LiAlO_2$) generated in the slag mineralogy during the treatment of LCO batteries can be recovered by flotation.

Nevertheless, these findings could not be replicated on NMC batteries. The German PyroLith project demonstrated that the presence of Manganese promotes amorphous phases; therefore, $LiAlO_2$ precipitation needs low cooling rates. Immobilising lithium into a $LiAlO_2$ phase favours its recovery through a flotation process before hydrometallurgical treatment, avoiding these problems and reducing processing volumes[3,5,6]. Engineering of artificial minerals (EnAM) overcomes these difficulties through controlled segregation and strategic crystallisation, producing mineral phases that can be separated by other means[7]. This is the case of LIBs, where the aim is to maximise the formation of $LiAlO_2$ for subsequent separation via flotation. EnAM, on a large scale, requires one unit to treat LIB material and another to ensure a low control cooling of the produced slag material. Figure 1 shows the finding of Li-based EnAM created under cooling conditions of 25°C/h in terms of lithium immobilisation into the $LiAlO_2$ mineral phase[5].

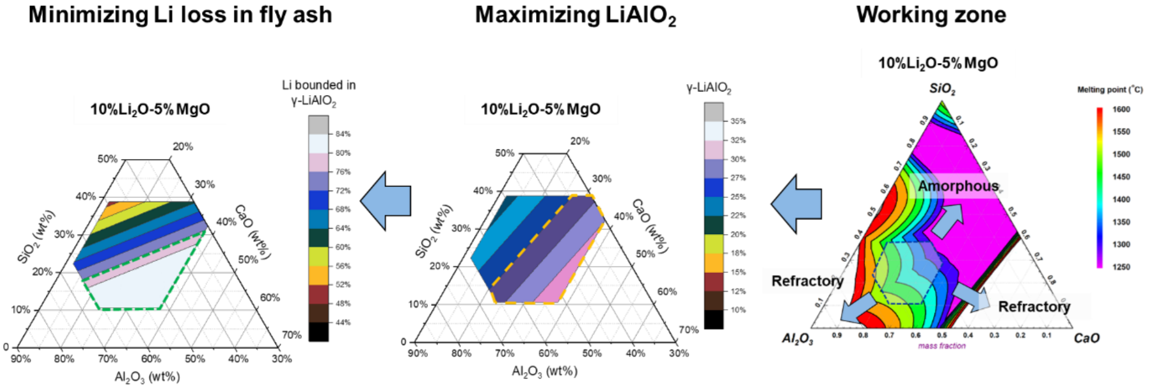

Figure 1: Optimisation of SiO_2-Al_2O_3-CaO-10%Li_2O-5%MnO mineral matrix to promote the immobilisation of lithium into $LiAlO_2$ under low cooling conditions[5].

Materials and Methods.

The treatments of 128,5 kg of pyrolysed black mass (BM) from the recycling of NMC LIBs provided by Accurec Recycling GmbH (composition in Table 1) was carried out in a Midsize Top Blown Rotary Converter (TBRC) with a 300 l vessel (100 l working volume), operating with natural gas and oxygen and equipped with FTIR system for gas analysis.

Table 1: Chemical composition of EoL Pyrolyzed NMC LIB black mass (BM) in weight percent.

Al	Cu	Mn	Fe	Ni	C	Li	Co	P	F	Cr	S
4.6	2.5	9.5	2.7	14.2	26.8	4.2	10.8	0.6	2.3	0.5	0.1

In addition to the battery BM material, 11.5 kg of quartz (Quarzwerke GmbH, Frechen, Germany), 17.2 kg of calcined lime (Weissfeinkalk CL 90, Dyckerhoff GmbH, Germany), 35 kg of Al_2O_3 (Almatis GmbH, Germany), and 8 kg of CuO (Lomberg GmbH, Germany) were utilised during the processing for the slag formation and the control of the metal phase melting point through the reduction of CuO into metallic copper using the graphite present in the batteries[2]. To deal with the graphite from the BM, which represents 27%, a combustion lambda of 1.05 (stoichiometric excess oxygen) was used during the process.

After treating the material in the TBRC at temperatures around 1500°C, the molten material was transferred to a temperature-controlled electric furnace (Thermo-Star GmbH) previously preheated to 1450°C and then cooled at a rate of 25°C/h using a clay–graphite crucibles type A20 from Atlantic Schmelztiegel GmbH (Germany).

Previous small-scale experiments demonstrate that this cooling rate was enough to fully crystallise slags rich in manganese and lithium oxides. Chemical composition of starting materials, metals, slags and flue gas restudies analysed using a “Spectro CIROS Vision” inductively coupled plasma-optical emission spectrometer (ICP-OES) SPECTRO Analytical Instruments GmbH, Kleve, Germany. Based on a combustion method, carbon analysis was performed using an “ELTRA CS 2000” system made by ELTRA GmbH, Haan, Germany.

X-ray diffraction (XRD) measurement is used to determine and quantify the different phases in the slag through an Empyrean diffractometer (Malvern Panalytical, The Netherlands). Rietveld analysis using the open-source software package Profex/BGMN version 5.1.0 is applied for the quantitative phase determination.

Results and Discussion

For the treatment of black mass (BM) material, 200 kg of material, including additives, were loaded, and between the preheating, loading and processing of the material, 9 hours were needed, consuming 7 kWh/kg of energy (5.7 kWh/kg for the processing) where 60% was provided by the burner running on natural gas and oxygen. The rest is electricity consumed by sensors, actuators, and engines (furnace rotation, scrubber, and exhaust system). These data have been summarised in Table 2.

Table 2: Summary of energy, inputs and outputs of the smelting campaign in TBRC.

	Preheating	Processing	Inputs		Outputs	
Total	1,3 kWh/kg	5,7 kWh/kg	Nat. gas	155,6 m^3	Sack filter	1,0 kg
Burner	56%	61%	Oxygen	77,5 m^3	Cyclone	0,1 kg
Rotation	1%	1%	Electricity	554 kWh	Slag	102 kg
Ventilation	30%	28%	Fluxes	71,7 kg	Metal	38 kg
Scrubber	14%	10%	BM	128,5 kg		

Continuous records of the emissions, gas flow temperature, and the proportions of particles emitted were kept during the process. Figure 2a shows a picture during the discharge stage of a controlled cooling unit. Figure 2b shows a schematic of all connections and control points (blue lines) of the Midi TBRC pilot plant installed at IME-RWTH Aachen University.

Around 38 kg of metal was collected after the process. Table 3 shows the chemical composition of the metal. It is estimated that about 4 kg may have been left in residual form inside the furnace. Considering the slag chemical composition (Table 4), reduction efficiency (metal) was 99% for Cu, Ni, and Co, 93% for Fe and 25% for Mn.

Table 3: Chemical composition of metal phase generated during the smelting in TBRC.

Co	Cr	Cu	Fe	Li	Mn	Ni	Si	Sn	C
28.5%	0.97%	25.2%	8.8%	0.01%	5.5%	36.5%	0.01%	0.36%	0.10%

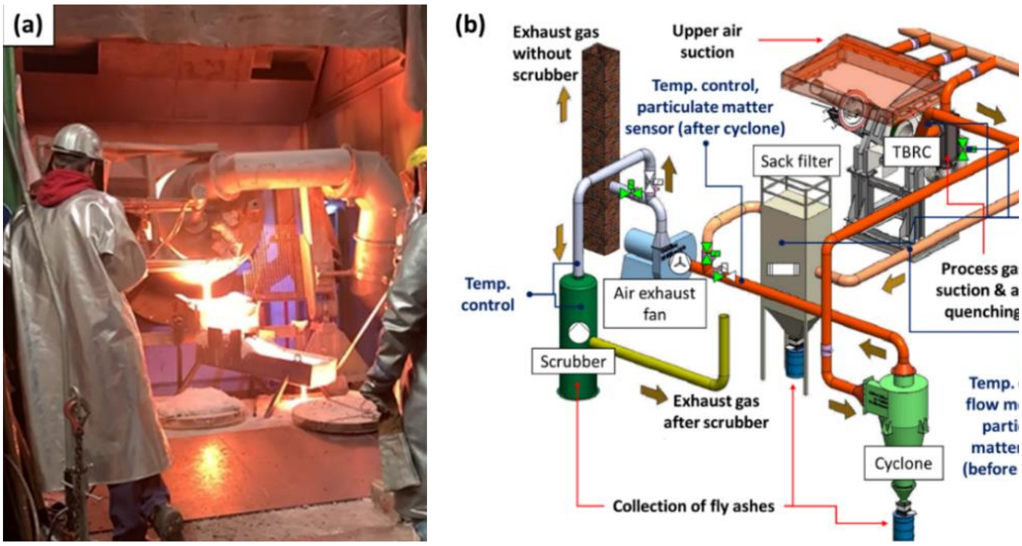

Figure 2: IME midi-TBRC setup is connected to the control cooling unit, (a) tapping after processing black mass, and (b) the exhaust system.

Table 4: Chemical composition of slag phase and fly ashes (sack filter and cyclone).

Samples	Cu	Ni	Mn	Ca	Si	Li	Al	Cr	Co	Fe	Na	C	S	F
	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Sack filter	4.4	1.0	0.7	3.3	1.2	0.5	1.7	0.3	0.4	3.7	0.9	5.4	0.4	--
Cyclone	1.2	0.7	0.6	4.7	0.7	0.2	3.9	0.3	0.3	4.0	0.4	2.3	0.8	--
Slag	0.1	0.1	6.6	10.1	5.8	3.7	26.5	0.7	0.1	0.3	0.1	0.1	0.0	0.8

Concerning the slag, it is estimated that 30% of lithium and 75 % of fluor were fumed during the process and ended up as fly ash collected between the cyclone, sack filter and scrubber (part of the lithium is in solution). Table 5 shows the mass distribution of lithium before and after the pyrometallurgical treatment.

Table 5: Mass distribution of lithium throughout the process.

BM (input)	Slag	Metal	Sack filter	Cyclone	Scrubber*	Lost in furnace*
5.4 kg	3.8 kg	4 g	5 g	20 g	1.4 kg	160 g

*It is estimated that 10% of the slag will be lost in the furnace attached to the refractory, and the rest of the lithium precipitates inside the scrubber.

As can be seen in Figure 2a, after the processing of the black material, the molten material was melted in a second electric furnace with controlled cooling at 25°C/h or in a metal bucket for uncontrolled cooling. Table 5 shows the mineral composition obtained after remelting and slow cooling at 25°C/h of 25 kg of the slag obtained in the large-scale test, which needed around 1.5 kWh/kg. Interestingly, the crucible, which contains a mixture of alumino-silicates and graphite, transferred silicon and aluminium oxides to the slag. This decreased the production of lithium aluminates ($LiAlO_2$), favouring the increase of Gehlenite and Al-Spinel. Nevertheless, even with this effect of contamination of the crucible elements, 78% of the lithium immobilised in the slag was transferred to a mineral phase that could be potentially recovered and enriched by flotation.

Table 5: Mineral composition of the slag phase and estimated bounded lithium.

Li bounded →	$LiAlO_2$	Eucryptite	Gehlenite	Al-Spinel	$LiMgMnSiO_4$	Quartz	Cuspidine	Fluorite
	17.9	2.3	33.2	29.4	10.7	0.4	5.6	0.4
	78%	5%	< 1%	< 1%	17%	< 1%	< 1%	< 1%

Figure 3 shows a section of the EnAM created from the BM treatment. $LiAlO_2$ exhibits a green fluorescence, which distinguishes it from other mineral phases, as demonstrated by Marko Ranneberg et al. In this experiment, the $LiAlO_2$ crystals have an ideomorphic structure with grain sizes of around 1 mm[6,8].

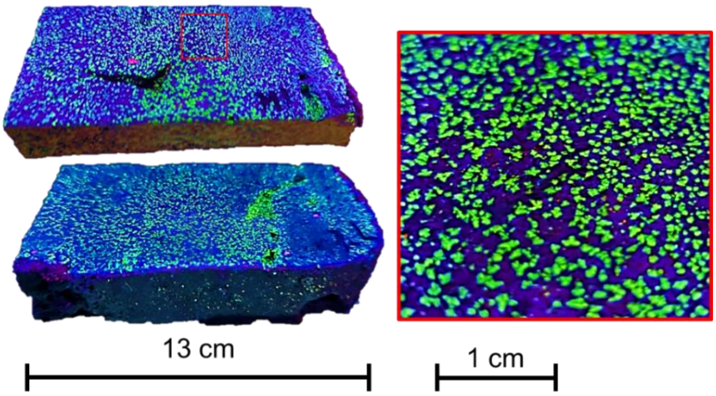

Figure 3: Li-based EnAM under 254 nm-UV light ($LiAlO_2$ is the green phase).

Several partners of the Pyrolith project already demonstrated that $LiAlO_2$ inside these EnAM from NMC battery recycling can be liberated and floated using Sodium oleate solutions with efficiencies up to 85% when the EnAM has a low amorphous content, and the particles are comminuted below 100 µm[3,9,10]. This EnAM produced from BM in large-scale assays is expected to show similar results to those already obtained with other samples processed under similar cooling conditions and mineralogy.

Conclusions

Even if in this work only one test is presented, there were three large-scale tests using LIBs material carried out with similar results demonstrating that not only metal recovery can be maximised for Co, Cu, and Ni but also lithium under the EnAM strategy can be immobilised into a mineral phase which facilitates its subsequent recovery by combining flotation and hydrometallurgical treatments without the risk of silica gel formation. Evaluating the pyrometallurgical route of lithium batteries employing Life Cycle assessment is a challenge for the scientific sector due to the lack of large-scale experimental data for the treatment of lithium batteries, either because large-scale results are not being published or laboratory tests are far from industrial reality. These semi-industrial scale tests are a more realistic source of information on the energy needs and emissions generated during the pyrometallurgical treatment of lithium batteries.

Acknowledgements

The authors acknowledge the financial support of the German Federal Ministry of Education and Research (BMBF) within the cluster project, “greenBatt PyroLith” (Grant No. 03XP0336B) and the German Research Foundation within the priority program “Engineered Artificial Minerals (EnAM)—a geo-metallurgical tool to recycle critical elements from waste streams” (Grant No. 470552553).

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