

Modeling, simulation and technical assessment of spent Li-ion batteries recycling plant



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Introduction

Based on the current tendency it is estimated that on global scale the LIBs industry will reach in 2026 the capacity of 1000 GWh corresponding to almost USD 140 billion which is almost four times the value reported in 2019 and only half of the capacity predicted for 2030 [1, 2]. It is undeniable that LIB production is on an ascendant trajectory, increasing from year to year in correlation with other industrial sectors, which boosts energy and raw material consumption to a level that clearly cannot be economically sustained by current supplies without a proper recycling [2]. Besides the deepening gap between demand and supply, generated by the increase of raw materials uncertainty and unavailability, there is a new challenge on the horizon associated with the accumulation of an estimated 300 million ton of spent LIB (SLIB) in the next 20 years [3].

Despite the large number of novel recycling approaches published recently the majorities of studies are performed only at laboratory level and deal with the processing of different material fractions from SLIB without offering an overall solution that can be deployed for industrial application.

The current study comes to close this gap by providing a quantitative assessment of various process concepts designed for the treatment of the complete SLIB. Process flow modeling software was used to evaluate the contribution of all process steps and equipments to the overall energy consumption and to the mass balance data required for the technical assessment of the large-scale recycling plant. To underline the advantages and identify the optimal novel process concept several key performance indicators were determined such as recovery efficiency, specific energy/material consumptions, specific CO₂ emissions, etc.

Results @ Discussion

The process is divided into the following subsystems (the PFD developed in CHEMCAD is presented in Fig. 1):

- 1 - The mechano-thermal treatment of LIBs
- 2 - Dissolution and purification
- 3 - Separation and recovery of manganese
- 4 - Dissolution of magnetic metals
- 5 - Separation and recovery of cobalt
- 6 - Separation and recovery of nickel
- 7 - Separation and recovery of lithium.

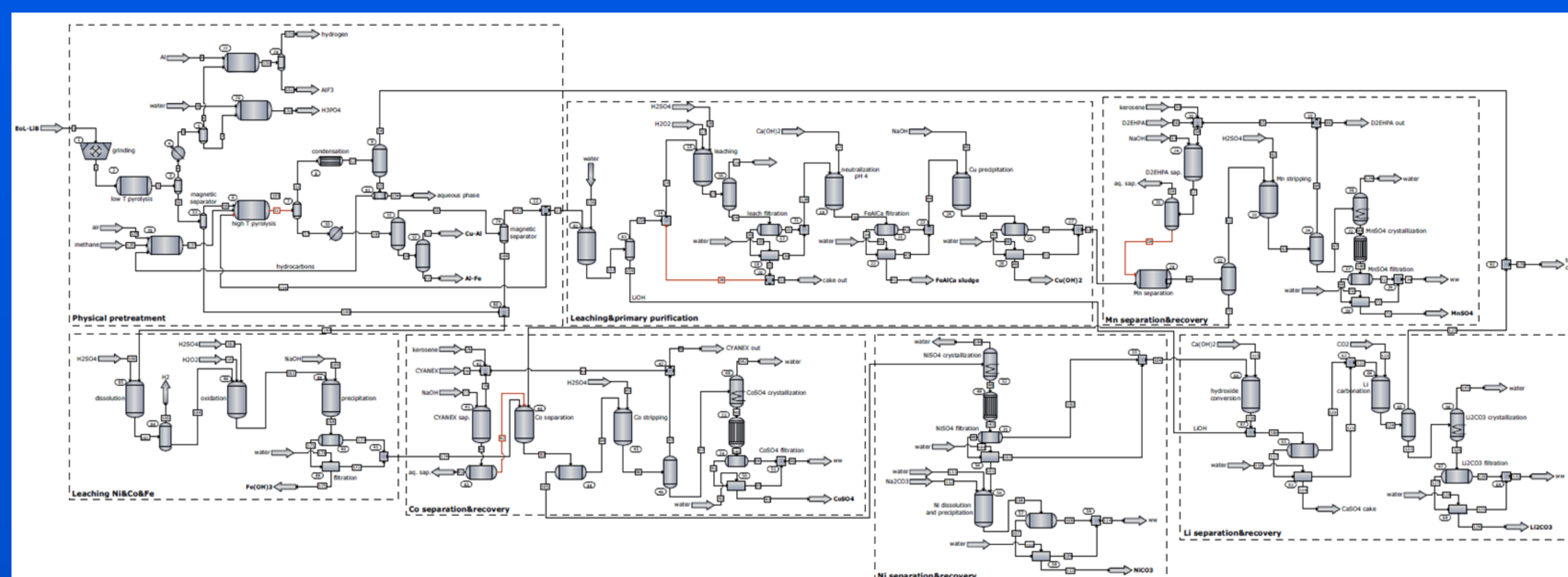


Fig. 1. Process flow diagram of the spent Li-ion batteries recycling plant.

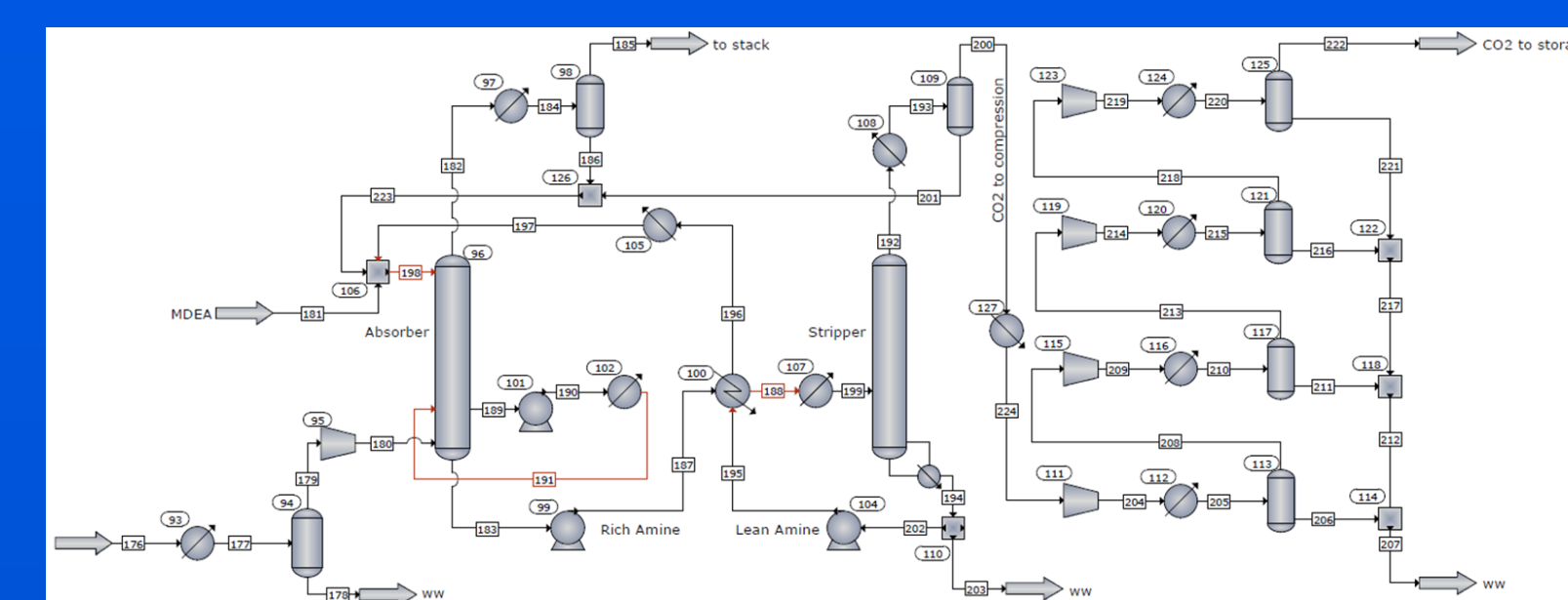


Fig. 2. PFD for the CO₂ capture process.

Considering the importance of CO₂ capture in the industrial sector, the recycling plant of spent LIBs was coupled with a post-combustion CO₂ capture based on amine absorption process (the PFD developed in CHEMCAD is presented in Fig. 2).

The evaluation of the technical performances for the recovery processes of metals from spent LIBs based on the defined mathematical models were carried out by simulating and optimizing the processes using process flow modeling software CHEMCAD specific to chemical engineering.

In order to identify the optimal systems for metal recovery from spent LIBs, the technical performances of the thermally integrated/non-integrated technological variants, respectively with and without CO₂ capture, were compared. In addition, the impact of the type of reducing agent (H₂O₂, C₆H₈O₇, HCOOH and H₂C₂O₄) on the performance of the spent LIBs recycling plant was assessed.

For the evaluation of the technical performances of the process the following cases were considered:

- Case I - thermally non-integrated process - to generate the thermal energy requirement, combustion of additional amounts of CH₄ was considered
- Case II - thermally integrated process - with H₂ combustion
- Case III - integrated thermal process with recirculation of CO₂ and water into the process.

Table 1. Recovery yields (in %) and production rates (in kg/h) for the main products of the spent LIB recycling process.

Product	MnSO ₄ ·H ₂ O	CoSO ₄ ·7H ₂ O	NiCO ₃	Li ₂ CO ₃	Fe(OH) ₃	Graphite	Al	Cu
Production rate	206.63	299.03	208.76	131.81	98.77	189.71	296.25	101.5
Recovery yield	84.09	79.26	82.61	94.84	98.21	87.50	93.24	90.91

Table 2. Specific consumption of raw materials in kg/kg LIB for the spent LIB recycling process.

Raw material	H ₂ O	CH ₄	H ₂ SO ₄	Na ₂ CO ₃	NaOH	air	Ca(OH) ₂	CO ₂	TOTAL
Consumption	2544	120	1019.7	211.98	424.76	3500	137	98.5	-
I	1.94	0.09	0.78	0.16	0.32	11.39	0.10	0.07	14.85
II	1.94	0.09	0.78	0.16	0.32	2.66	0.10	0.07	6.17
III	1.10	0.09	0.78	0.16	0.32	2.66	0.10	0	5.22

Table 3. Specific consumption of raw materials in kg/kg product for different subsystems of the spent LIB recycling process using oxalic acid.

Subsystem	1	2	3	4	5	6	7
TOTAL, kg/h	4959.5	801.86	727.10	1145.69	693.60	861.98	272.50
W, kg/kg	3.77	2.08	3.52	4.61	2.32	4.13	2.07

References

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Table 4. Thermal energy balance for the spent LIB recycling process using oxalic acid.

Subsystem	Parameters of energy flows	Thermal energy generated			Thermal energy consumed			TOTAL consumption, MJ/h	Specific consumption, MJ/kg	Equivalent consumption, kg CH ₄ /h
		1	2	3	1	2	3			
1	T, °C	120	40	380	370	797		1249	0.95	25
	Q, MJ/h	-488	-51	-11269	1173	76				
2	T, °C	60						0	0	0
	Q, MJ/h	-1704								
3	T, °C	24			24	40	25	2159	10.45	43
	Q, MJ/h	-1687			1469	271	419			
4	T, °C	32			40			700	2.82	14
	Q, MJ/h	-1713			700					
5	T, °C	24			24	40	25	7023	23.49	140
	Q, MJ/h	-1395			1384	5057	582			
6	T, °C	40	110		110			2129	10.20	43
	Q, MJ/h	-258	-583		2129					
7	T, °C	35			93			387	2.94	8
	Q, MJ/h	-112			387					
I								13646		273
	T, °C	380			370	797				
II	T, °C	380			370	797		1249	0.95	25
	Q, MJ/h	-3781			1173	76				

Table 5. Total and specific CO₂ emissions, respectively the average energy consumption of the CO₂ capture process for the recycling of spent LIBs.

Process type	I		II		II with H ₂ combustion		II with H ₂ combustion and partial reuse of CO ₂ in the process	
	Total, kgCO ₂ /h	kg CO ₂ /kg LIB	Total, kgCO ₂ /h	kg CO ₂ /kg LIB	Total, kgCO ₂ /h	kg CO ₂ /kg LIB	Total, kgCO ₂ /h	kg CO ₂ /kg LIB
H ₂ O ₂	1402	1.07	652	0.50	516	0.39	417	0.32
C ₆ H ₈ O ₇	1418	1.08	667	0.51	517	0.39	418	0.32
HCOOH	1425	1.08	675	0.51	525	0.40	426	0.32
H ₂ C ₂ O ₄	1449	1.10	698	0.53	548	0.42	449	0.34
CO ₂ capture energy consumption GJ/h	4.73		2.24		1.75		1.42	

Conclusions

- Based on the energy balance data it can be concluded that the process remains a thermal energy generator even with CO₂ capture, producing 1.5 GJ/h for thermally integrated process, ~2 GJ/h for thermally integrated process with H₂ combustion and 2.3 GJ/h for thermally integrated process with H₂ combustion and partial reuse of CO₂
- As an overall conclusion it can be stated that the technological option with H₂ combustion and partial reuse of CO₂ is the most efficient in terms of recycling spent LIBs regardless of the reducer used.

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