Simulation of a Hydrometallurgical Battery Recycling Process via HSC Sim

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Abstract

The growing demand for electric vehicles is a consequence of the introduction of strictly reduced emission requirements, which are driving the global automotive industry towards a sustainable future. Consequently, there has been an increase in the manufacturing of Li-ion batteries to meet the growing demand. As the number and variety of LIBs in production increase, concerns about their environmental impact and the scarcity of raw materials used in their manufacture also increase. The circular economy is therefore aimed at closing the material loop by recycling end-of-life batteries. However, the current recycling capacities are insufficient, and current research is either limited to laboratory scale or unable to achieve benchmark recovery efficiencies. The objective of this study is to promote Li recovery, increase purity of other metals and to digitalise a hydrometallurgical battery recycling process in order to facilitate the testing of new ideas at an earlier stage, prior to laboratory-scale trials, or to assess the feasibility of new concepts. This consequently enhances the flexibility of the process. In order to achieve this objective, a simulation of the early-stage lithium recovery (ESLR) process, acid leaching, and selective precipitation was created by using HSC Chemistry software. In addition to facilitating the testing new ideas, the digitalised process allows for the minimisation of Li loss, reduction of hazardous chemicals, minimisation of waste streams, and lowering of water consumption. This is accomplished by adapting cascade leaching process into an ESLR process and an acid leaching process, where the process water was recirculated within the process. The simulation was validated through experimental work. Consequently, although there are differences, there is a correlation between the digital twin and the experimental results, indicating that the digital twin is a

valuable tool for optimising the recycling process. The reasons will be discussed and recommendations given.

1 Introduction

As governmental regulations aimed at reducing carbon emissions, the global demand for EVs is growing, consequently the volume of end-of-life LIBs is also increasing dramatically. [1-3] The recycling of LIBs presents both challenges and opportunities. The critical materials contained within these batteries such as lithium, cobalt, nickel, and manganese are limited resources that require sustainable management methods. [4, 5] Current recycling efforts often struggle to recover these valuable materials efficiently while minimizing environmental impact. [6] The integration of digitisation and simulation is essential to advance process metallurgy towards a circular economy. Gaining insights into metal distributions within the system requires relevant data covering physical, metallurgical and thermodynamic aspects. Furthermore, simulation is a key tool in determining recycling rates, allowing accurate calculations of material-specific recycling efficiencies, taking into account design parameters. This approach is essential for developing industrial processes, optimising mass transfer, and comprehending reaction kinetics and thermodynamics. All these capabilities are enhanced by utilizing software tools such as HSC Sim. [7] In response to these challenges, this study aims to develop a hydrometallurgical recycling process with re-circulated process water and to test this first in a model process created by HSC Chemistry software. This approach focuses on early-stage lithium recovery (ESLR), acid leaching, neutralization and precipitation of NMC while integrating innovative methodologies designed to minimize waste generation and enhance material recovery rates. [8]

2 Methods and Materials

2.1 Experimental Materials

Prior to experiments the black mass went through a chain of pre-treatment processes. The black mass comes from end-of-life consumer cells with primarily NMC cathodes, which were subsequently discharged and then industrially pyrolyzed in a vacuum batch furnace. The active mass comes from 4 batches, all of which have reached a maximum temperature of approximately 550 ºC in the batch core. The furnace was inerted with N_2 before pyrolysis, then pyrolysis gas atmosphere and low barrier gas flow N_2 at 800 mbar pressure, after the heating phase the pressure was lowered to 200 mbar for 30 min. Afterward, the batch was cooled in the furnace in an inert atmosphere. Mechanical separation after cooling is then took place. The processes are, firstly, granulator then flip-flow screen and lastly overbelt magnet to separate the cell housings. Consequently, the obtain black mass has <1 mm particle size.

2.2 Experimental Method

The methodology employed in this research consists of several key steps designed to decrease wastewater consumption and increase Li recovery efficiency, as well as the purity of NMC precipitates. The flowchart of the process is depicted in Figure 1, in which the green colour represents a new approach in the process. Prior the experimental work, a comprehensive simulation of the shown process was created using HSC Chemistry 10. The equilibrium calculations and simulation tools were mainly used for this purpose.

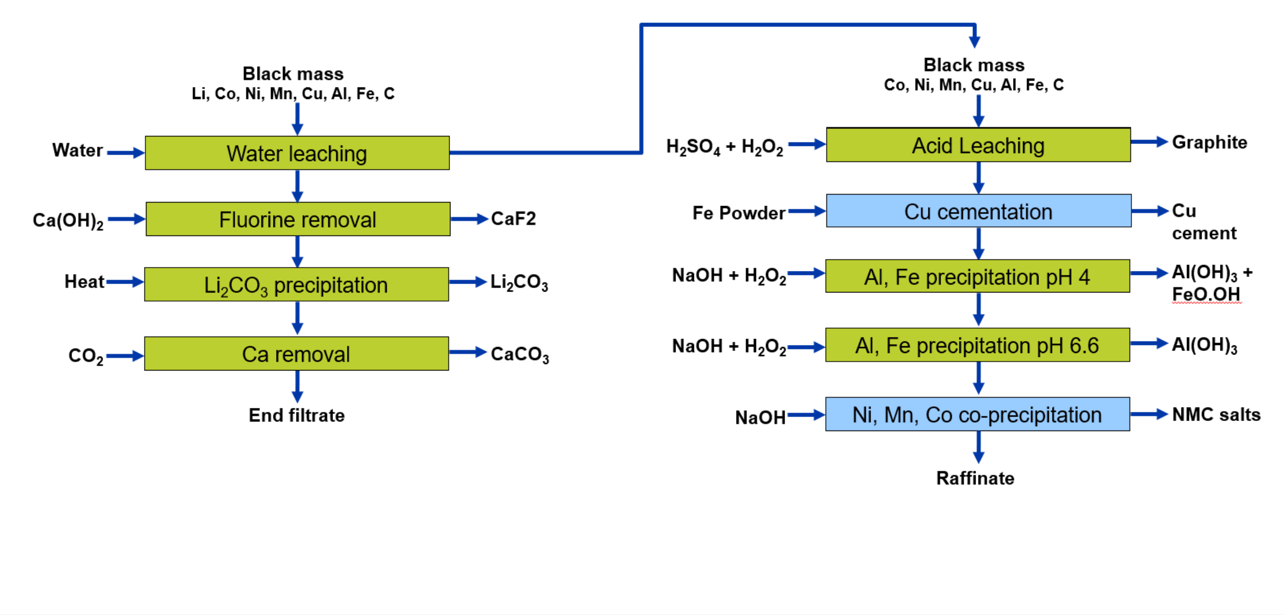


Figure 1: Applied process flow chart

Rather than beginning with acid leaching and dissolving all the elements in the black mass, the ESLR method was utilized, where the black mass is leached with water at room temperature. Subsequently, a fluorine removal step has been adapted to remove co-leached F ions and promote Li purity at the product. This is followed by lithium carbonate precipitation by applying heat only to decrease the solubility since the solubility behavior of Li_2CO_3, which exhibits solubility of 13.3 g/L at 20 ºC and 7.2 g/L at 100 ºC [9]. And then calcium removal was conducted to remove impurities and thus preventing them to recirculate. Following the completion of these four processes, the process water is re-circulated with the aim of creating a counter-current cascade leaching process. And this cascade leaching is consisted in total of 3 cascades containing these 4 steps. One of the cascade flow sheet simulated is shown in Figure 2.

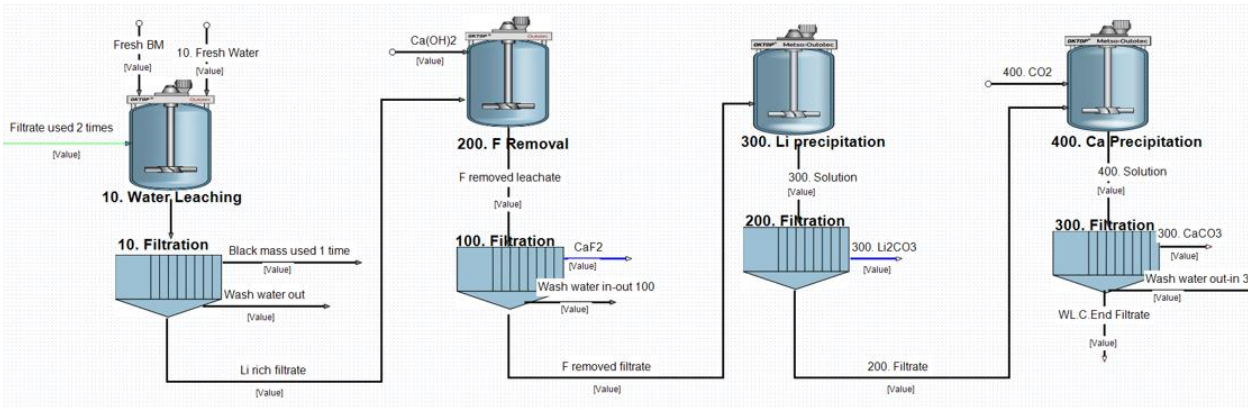


Figure 2: The first cascade part of the process on the simulation

The next step was conventional acid leaching using sulfuric acid and hydrogen peroxide employing a two cascade leaching approach. The application of acid leaching cascade flow chart is shown in Figure 3. Cascade leaching on simulation was continuous process, however in practical work this is not possible. Consequently, the method presented was adopted to establish a continuous process. The implementation of the acid leaching cascade was carried out to effectively dissolve the remaining metals from the pre-leached black mass through optimised conditions such as pH control, temperature at 80 ⁰C and reaction time of 2 hours.

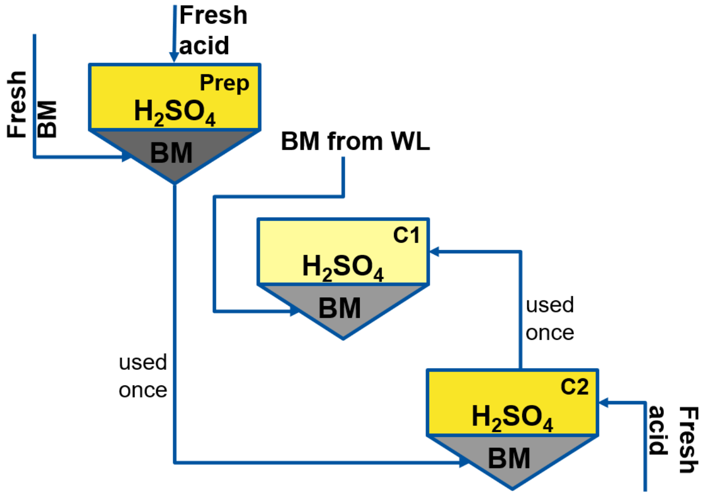
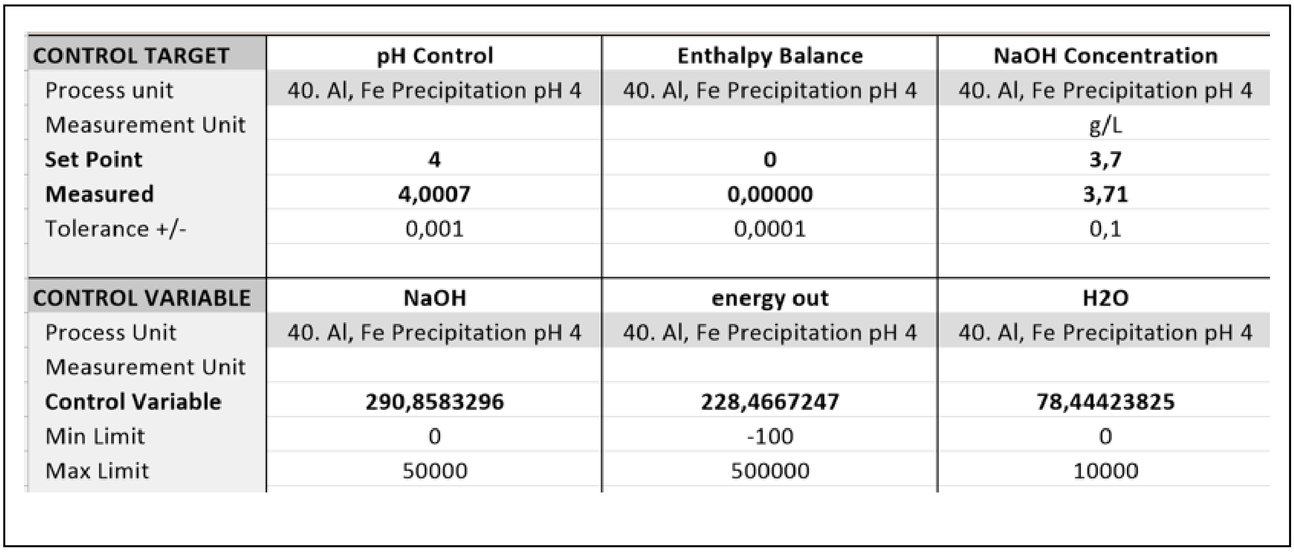


Figure 3: Flow chart of cascade leaching application at the experiment

This was followed by solution neutralization processes. The Fe-Al precipitation was performed in two subsequent steps for higher selectivity both at 60 ºC. In the initial step at pH 4, the objective is the precipitation of Fe along with a proportion of Al. Subsequently, at a pH of 6, the residual Al is precipitated. This approach was adopted to prevent the loss of MHP (metal hydroxide precipitates) in the preceding steps. NaOH was added drop by drop to control the pH at the experiment whereas, on the simulation, the control panel was used to manage the pH value and NaOH concentration as it is given in Figure 4. As the final stage of the process, NMC precipitation was conducted at pH 10.4.



CONTROL TARGET	**pH Control**	**Enthalpy Balance**	**NaOH Concentration**
Process unit	40. Al, Fe Precipitation pH 4	40. Al, Fe Precipitation pH 4	40. Al, Fe Precipitation pH 4
Measurement Unit			g/L
Set Point	**4**	**0**	**3,7**
Measured	**4,0007**	**0,00000**	**3,71**
Tolerance +/-	0,001	0,0001	0,1
CONTROL VARIABLE	**NaOH**	**energy out**	**H2O**
Process Unit	40. Al, Fe Precipitation pH 4	40. Al, Fe Precipitation pH 4	40. Al, Fe Precipitation pH 4
Measurement Unit			
Control Variable	**290,8583296**	**228,4667247**	**78,44423825**
Min Limit	0	-100	0
Max Limit	50000	500000	10000

Figure 4: Simulation controls example for Al-Fe precipitation at pH 4

3 Results and Discussion

The simulation and experiment results are given in Figure 5, on the left hand-side the amount of the ions in mg is given, and on the right hand-side the leaching efficiency of Li and F from cascades one, two and three. As it can be seen on the figure, the amount of Li and F ions are aligned in C1 and C3 both in simulation and experiment. However, this can not be observed at C2. At C3, Li-poor black mass is leached with fresh water and most of Li and F are dissolved successfully in the simulation unlike the experiment. And these ions are carried onto C2. The efficiency difference leads to have greater difference in the amount of the ions at C2. In principle, the difference can be also attributed to the preparation steps for the experiment as it is mentioned for the acid leaching cascade because the same black mass does not circulate from C3 to C2. Consequently, this leads to the difference of ion amounts at C2. Moreover, the simulation results demonstrated an overall lithium leaching efficiency of 91.9 % across all stages of the simulation, and at experiment this was 67.4 %. Notably, during the water leaching cascades, lithium concentrations showed significant increases in subsequent filtrates, while the fluorine content decreased substantially following treatment with $Ca(OH)_2$.

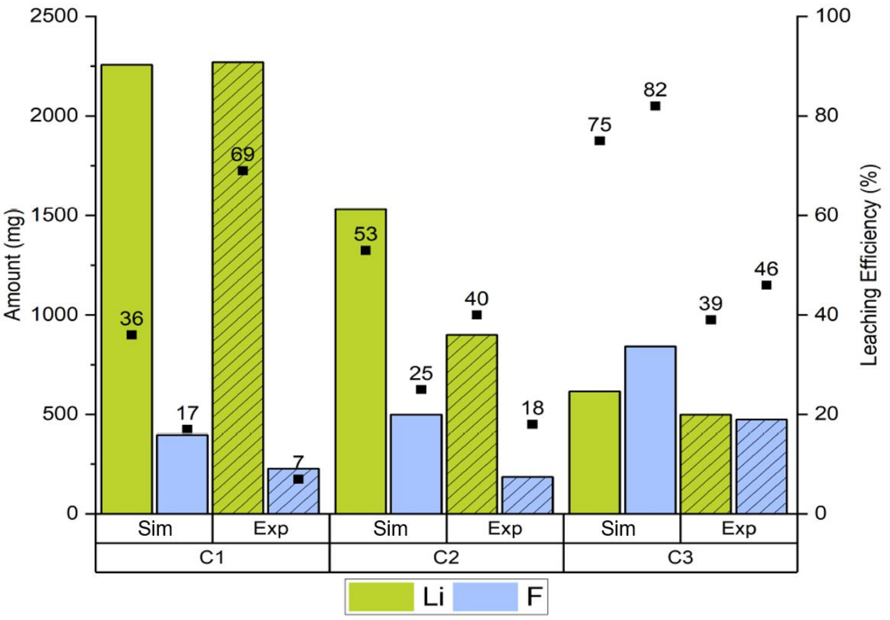


Figure 5: A comparison of the simulation and experiment results for water leaching cascade

During acid leaching in both simulation and experiment, all the remaining elements were leached after the second cascade. Additionally, successful precipitation outcomes were achieved for various metals, including copper, which exhibited a remarkable recovery rate exceeding 99 % in both simulation and experiment. The results from Fe-Al precipitation and NMC precipitation are given in Figure 6, where it is shown based on the pH value. Each colour represents the pH value and how much of the particular element precipitated in which pH value. In the initial stage of Fe-Al precipitation at a pH of 4, 99.4 % of the Fe is precipitated, along with 84.4 % of the Al in the simulation. Whereas, it resulted in 98 % Fe, 61.6 % Al in the experiment. Subsequently, at the second stage of the process (pH 6.6), the remaining aluminium is also successfully precipitated in the simulation. Conversely, a complete Al precipitation was not observed in the experiment. Furthermore, during this step, co-precipitation of several metals was observed in both the experiment and the simulation. Specifically, the experiment yielded 35 % Co and 7.5 % Mn co-precipitation, while the simulation resulted in 96.5 % Co. In the final stage of the process, NMC precipitation at a pH of 10.4 was carried out, resulting in the precipitation of the remaining metals.

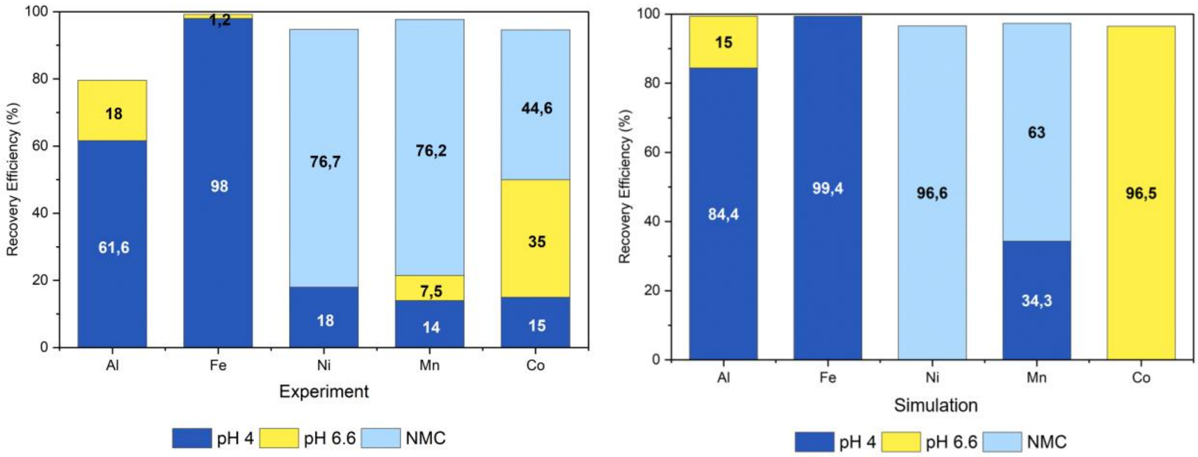


Figure 6: A comparison of precipitation steps based on the precipitation pH value

This discrepancy between the simulation and experiment results can be primarily attributed to the differences in procedure encountered in the laboratory experiments compared to the predictions made by the simulations in creating the counter current leaching cascade. In the simulation the leaching cascade is a continuous process, whereas in the practical work continuity was not accomplished. Furthermore, the discrepancy between the ion concentrations as predicted by the simulated models and the actual experimental results highlighted several challenges associated with real-world implementation.

4 Conclusion and Outlook

This study developed a process simulation that closely mirrors real-world hydrometallurgical battery recycling processes, while achieving high overall material recovery efficiencies. However, a significant difference between simulated and experimental results requires further investigation to optimise laboratory protocols:

- Inconsistencies observed in leaching efficiencies indicate potential areas for improving preparation methods or enhancing dissolution kinetics.

- In order to minimise material loss during precipitation steps, it is possible to automate pH control, thus preventing the occurrence of application errors.

- Future research should explore alternative strategies for managing co-products generated throughout various stages such as calcium carbonate, iron hydroxide, including reusing filter cakes and wash water for optimising chemical usage, to improve sustainability associated with LIB recycling efforts.

Ultimately, this research highlights not only the viability but also the necessity of adopting advanced modelling techniques like digital twins for improving resource efficiency within circular economies focused on critical materials such as those found in LIBs.

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