OPTIMIZED LITHIUM, COBALT, and NICKEL RECOVERY FROM BATTERY WASTE USING SOLVENT EXTRACTION

By

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ABSTRACT

This study introduces a database of commercial materials developed for solvent extraction of lithium, cobalt, and nickel: D2EHPA and Cyanex 272. The database contains thermochemical/physical properties, speciation, and activity coefficient parameters for the extractants, their complexes, and the organic solvent. The model predicts the nickel and cobalt extraction performance as a function of the separation pH, temperature, solvent-pregnant liquor (PL) mixing ratio, separation efficiency, extractant concentration in the diluent, and number of stages. The validated model was then used to optimize the operating conditions of the SX units in order to maximize the extraction efficiency while minimizing the co-extraction of impurities.

Next, the developed database was used to simulate a generic hydrometallurgical battery recycling process. The process includes leaching of metals from the spent lithium ion battery, separating metals into a pregnant liquor, extracting Co and Li using D2EHPA and Cyanex 272, and stripping the metals from the organic phase. The model predicted the nickel and cobalt extraction performance as a function of the separation pH, temperature, solvent-PL mixing ratio, separation efficiency, extractant concentration in the diluent, and number of stages. The validated model was then used to optimize the operating conditions of the SX units in order to maximize the extraction efficiency while minimizing the co-extraction of impurities. The simulation results showed that the introduced database can be used to reasonably predict the partitioning of Li, Ni and Co between the water and organic phases. When coupled with a process simulation software, it accurately predicted the heat, mass, and speciation balance among the separation units, and optimized the processes within the constraints of the existing operating conditions.

Keywords: Solvent extraction, D2EHPA, Cyanex 272, Battery recycling, hydrometallurgy, thermodynamic database, process simulation, phase partitioning, process optimization

INTRODUCTION

In the existing literature, there is a lack of a reliable thermodynamic model that could be incorporated into a process simulation tool to design, simulate, and optimize metal recovery during the solvent extraction (SX) process. The increasing demand for batteries, particularly lithium-ion batteries (LIBs) used in electric vehicles (EVs), portable electronics, and renewable energy storage systems, presents a great challenge for the future of critical materials. Battery recycling is needed to meet this demand. Given that battery recycling is required for the continued supply of critical materials, significant scientific advancements in recycling technology are needed for efficient and sustainable operations.

Solvent extraction is an economical option for producing usable, high-value species like lithium and cobalt. As a result, this work focuses on hydrometallurgical processes, like solvent extraction, that can selectively extract critical metals at ambient temperatures.

The development and scaleup of new technologies like SX rely on accurate and versatile modeling and simulation to perform feasibility studies and optimization of process flowsheets. There is presently, however, no reliable thermodynamic model that can be incorporated into a process simulation tool to design and optimize metal recovery during solvent extraction (SX). In this work, a solvent extraction database was developed to model the complex phase and chemical equilibria of liquid-liquid systems. This database, coupled with an MSE electrolyte model (activity model) enables optimization and scale-up of these emerging battery recycling processes.

The SX database was implemented in a process flow simulator to model SX and stripping with acid leaching, pH neutralization, separation, and thermal evaporation. The process model is used to maximize recovery and product purity and minimize chemical use.

THERMODYNAMIC MODELING OF LIQUID-LIQUID EXTRACTION

Thermodynamic modeling of solvent extraction, particularly for the extraction of Co, Ni, or Li, is performed using the MSE model.(1-3) Solvent extraction, also referred to as liquid-liquid extraction, is a separation process that involves two phases: an aqueous liquid in equilibrium with an organic liquid phase. Under such a liquid-liquid equilibrium (LLE) condition, the chemical potentials (μ_i^{LA}, μ_i^{LO}) of species *i* in aqueous *A* and organic *O* liquids are determined as

$$\mu_i^{LA} = \mu_i^{LA,0,x}(T,P) + RT \ln x_{A,i}\, \gamma_{A,i}^{x,*}(T,P,x)$$

$$\mu_i^{LO} = \mu_i^{LO,0,x}(T,P) + RT \ln x_{O,i}\, \gamma_{O,i}^{x,*}(T,P,x)$$

where $\mu_i^{LA,0,x}(T,P)$ and $\mu_i^{LO,0,x}(T,P)$ represent the standard-state chemical potentials of species *i* in each phase, estimated from the Helgeson-Kirkham-Flowers (HKF) equation of state.(4) The parameters $x_{A,i}$ and $x_{O,i}$ are the mole fractions of species *i* in the aqueous and organic phases, respectively. Lastly, $\gamma_{A,i}^{x,*}$and $\gamma_{O,i}^{x,*}$ represent the unsymmetrically normalized, mole fraction-based activity coefficients of species *i* in the aqueous and organic phases, respectively. The MSE activity coefficient model addresses the effect of solution nonideality in the aqueous phase, leveraging the excess Gibbs Energy model to account for long-range electrostatic, short-range intermolecular, and primary ionic midrange interactions.(5,6) The speciation calculation was made through a computational method that integrates the excess Gibbs Energy model with a formulation for the standard-state properties of each individual species. At equilibrium, the chemical potentials for each component *i* are equal in the two coexisting organic and aqueous phases, represented mathematically by

$$\mu_i^{LA} = \mu_i^{LO}$$

Due to the requirement of electroneutrality in electrolyte solutions, only the chemical potential of an electrically neutral salt is experimentally accessible, despite cations and anions existing as separate species. Therefore, in an aqueous phase containing a single cation *C* and a single anion *A*, the chemical potential of the electrolyte can be obtained as,

$$\mu_{C_{\nu c}A_{\nu a}} = (\nu_c \mu_C^0 + \nu_a \mu_A^0) + \nu RT \ln(\gamma_\pm x_\pm)$$

where ν_c and ν_a correspond to the valence charge of the cation and anion, respectively (2), and are calculated by

$$\gamma_\pm = \left(\gamma_C^{\nu_c}\,\gamma_A^{\nu_a}\right)^{\frac{1}{\nu}}$$

$$x_\pm = \left(x_C^{\nu_c}\,x_A^{\nu_a}\right)^{\frac{1}{\nu}}$$

and the LLE criterion can be computed according to:(2)

$$(\gamma_\pm x_\pm)^{Lo} = (\gamma_\pm x_\pm)^{LA}$$

for which the excess Gibbs Energy model was employed to calculate the activity coefficients in the organic and aqueous liquid phases.(2)

It is crucial to develop thermodynamic models for metal extraction pH isotherms to predict the distribution ratio, number of required extraction stages, and the overall SX process model. The speciation-based MSE thermodynamic framework computes the pH of mixed-solvent solutions, that can effectively reproduce properties such as solubilities, vapor-liquid equilibria, and solution pH.[7] Thermodynamic modeling of liquid-liquid systems exhibits greater sensitivity to binary ionic interactions than to vapor-liquid ones.(2) Thus, to enhance the accuracy of models in SX liquid-liquid systems without compromising the precision for the VLE calculations, the thermodynamic model includes middle-range interaction terms alongside classical UNIQUAC terms. These additional terms account for interactions between ions and neutral molecules during the SX process, which can enhance the model's predictive capabilities.

The thermodynamic framework in which the database is embedded uses standard-state properties including Gibbs Energy of Formation, entropy, and HKF equation parameters to determine the most thermodynamically favored ion pairs, complexes, LLE, etc. at different system conditions. The chemical potential of each species (equations above) is then obtained by integrating the standard state properties with an activity model that incorporates an ionic-strength-independent virial interaction parameter, UNIQUAC parameters, and temperature- or concentration-dependent middle-range interaction parameters. These interactions govern the behavior between Co/Ni-extractant complexes, the extractant, solvent, modifier, and other chemical components involved in the SX process.

The thermodynamic framework presented herein shows a substantial potential in handling LLE calculations and modeling the chemistry of the SX process involved in Co, Ni, and Li extraction during battery recycling processes. The following section will discuss various considerations regarding thermodynamic modeling of SX chemistry.

SPECIFIC CONSIDERATIONS FOR SOLVENT EXTRACTION DATABASE AND MODELING

There are numerous commercial extractants for hydrometallurgical extraction of Ni, Co, Li and other metals, with D2EHPA (Di(2-ethylhexyl) phosphoric acid) and Cyanex 272 (Bis(2,4,4-trimethylpentyl)phosphinic acid) being among the most commonly utilized. Typically, these extractants are mixed with an organic solvent (diluent), to boost the solubility of the metal-extractant complex in the organic phase. The diluent also serves as an equilibrium modifier, enhancing the selectivity of the extractant. These solvents need to possess specific physical properties, including low solubility in the aqueous phase, mutual miscibility with the extractant, low volatility, high solvency for the extracted metal complex, and a low affinity for interaction with the extractant/modifier.(8, 9) Although both aromatic and aliphatic solvents, could be used as diluent, their commercial use is often restricted by environmental constraints.

Kerosene is a cost-effective diluent for industrial-scale use. Different classes of commercial kerosene have been synthesized for hydrometallurgical applications, typically consisting of paraffinic, naphthenic, and aromatic hydrocarbons containing between 10 to 16 carbon atoms per molecule. Kerosene exhibits a wide range of physical properties, including a density of approximately 0.8 g/cm3, a boiling point ranging from 180 to 250°C, and a flash point of 70 to 85°C or higher. In certain cases, commercial sulfonated kerosene is used, resulting in reduced levels of unsaturated impurities, increasing the potential for enhanced metal extraction efficiency.(10) Therefore, it is useful to develop two chemistry models for kerosene, with one representing the lighter end or low-boiling kerosene, and the other representing the heavier end or high-boiling kerosene. These chemistry models offer a reasonable foundation for modeling the SX process, as the exact properties of the diluent may not be as critical as those of the extractants. Alongside the diluent, a phase modifier such as tri-n-butyl phosphate (TBP) or isodecanol may be added as a synergist to SX processes. These additives enhance separation and prevent the formation of a third phase by improving the solubility of the extractant and modifying interfacial properties.(11)

The SX database currently includes two commercial extractants, D2EHPA and Cyanex 272, four solvent, low- and high-boiling kerosene, iso-octane, toluene, and phase modifiers that are appropriate for separating Ni and Co from battery wastes. Creating the database entailed a detailed analysis of the underlying chemistry. This analysis involves examining the formation and thermodynamic stability of Ni/Co complexes, estimating the thermophysical properties of those complexes, studying extractant dissociation, and considering how these factors could potentially change with SX operating conditions, such as pH, temperature, ionic strength, metal, extractant, or solvent concentrations.

Typically, the quantification of each extraction stage in a SX model involves defining parameters such as the distribution coefficient (D_{Co} ,D_{Ni}), percent of metal extracted (E_{Co} , E_{Ni}), and separation factor, which is calculated by the ratio of the Co and Ni distribution coefficients ($\alpha_{Co,Ni}$):(12)

$$D_{Co} = \frac{Concentration\ of\ Co\ in\ L_O}{Concentration\ of\ Co\ in\ L_A}$$

$$D_{Ni} = \frac{Concentration\ of\ Ni\ in\ L_O}{Concentration\ of\ Ni\ in\ L_A}$$

$$E_{Co} = \frac{N_{Co,0} - N_{Co}}{N_{Co,0}} \times 100$$

$$E_{Ni} = \frac{N_{Ni,0} - N_{Ni}}{N_{Ni,0}} \times 100$$

$$\alpha_{Co,Ni} = D_{Co}/D_{Ni}$$

where $N_{Co,0}$ and $N_{Ni,0}$ represenet the initial moles of Co and Ni in the aqueous phase, and N_{Co} and N_{Ni} are the moles of Co and Ni in aqueous liquid after extraction. To achieve optimal extraction efficiency, it is necessary to adjust the process variables, such as the temperature, solvent-to-feed ratio, aqueous/organic (A/O) volume ratio, extractant and solvent concentrations, pH of the aqueous phase, the type of extractant(s), and the composition of the organic phase. Since commercially available extractants typically consist of large organic molecules, properties for many of these complexes are often unavailable. Thus, it became necessary to use estimation techniques to predict extractant properties.(13,14) It is also essential to account for phase equilibrium calculations related to the extractants and diluents, particularly their mutual solubility with water, to accurately simulate their separation in the organic liquid from the aqueous phase. For practical applicability, realistic modeling entails parameterizing the model to optimize the concentration of metal-extractant complexes in the organic phase. This involves developing parameters for interactions between Co-/Ni-extractant complexes and interactions among other species in the system.

DATABASE VALIDATION FOR SX PROCESS

The SX database was parameterized using available experimental data. Figure 1 shows comparisons between literature data and model predictions for Co, Ni, and Li extraction using Cyanex 272 and

D2EHPA in kerosene at different temperatures.[15-18] The model predictions demonstrate a reasonable level of consistency in reproducing the SX isotherms for these metals.

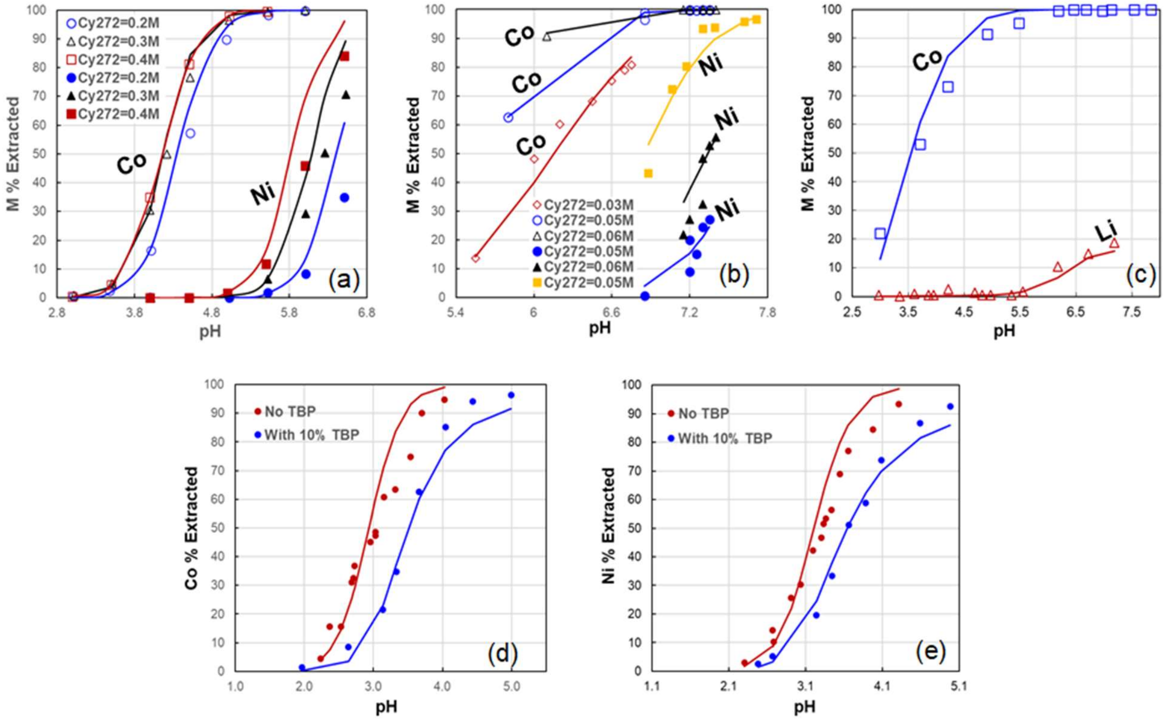

Figure 1. Model predictions (solid lines) vs. literature findings (data points) for percent extraction of metals in (a) 0.017M metal at different concentrations of Cyanex 272 in high-boiling kerosene at 40 °C, (b) 0.01M metal at different concentrations of Cyanex 272 + 0.18 M TBP in low-boiling kerosene at 30 °C, (c) 0.29M Co + 0.25 M Li + 0.64M D2EHPA in high-boiling kerosene at 25 °C, and (d, e) effect of TBP on Co and Ni extraction in solution containing 5 g/L metal + 20% D2EHPA in low-boiling kerosene at 30 °C.

As shown in Figure 1 (a) and (b), Ni extraction typically occurs at a higher pH compared to Co extraction, primarily because the extraction of one Co-Cyanex 272 complex is a dimer, meaning that the metal complexes with two Cyanex 272 molecules, whereas Ni complexes with three. In Figure 1, the percentage of metal extraction is seen to rise with greater concentrations of the extractant and at higher pH levels. This is because the increase in pH leads to changes in speciation by influencing the protonation/deprotonation of the functional groups on the extractant molecules. This process brings more metal ions into their soluble form, facilitating their interaction with the extractant molecule and thereby enhancing overall SX efficiency.[19,20] When using D2EHPA in high-boiling kerosene (Figure 1(c)), the extraction of Co experiences a rapid increase as the pH rises, particularly in pH levels below 5; complete Co extraction could be obtained when pH is greater than or equal to 6.5. However, Li extraction does not occur when the pH is below 5.5; instead, Li extraction into the organic phase is triggered at pH levels above 5.5. Figures 1 (d) and (e) illustrate the influence of TBP modifier on Co and Ni extraction isotherms, respectively. The presence of TBP modifier can enhance phase separation during metal extraction, as seen in Figures 1 (d) and (e); TBP leads to a shift in the isotherms to higher pH levels. This widening of the ΔpH gap improves the separation of Co from Ni in the subsequent SX steps. The MSE model reasonably captures these process behaviors during SX of Co, Ni, and Li.

BATTERY RECYCLING PROCESSES

The recovery of valuable metals from spent LIBs involves mechanical, thermal, and hydrometallurgical processes. The processes are complex and involve many possible process configurations including shredding, pyrometallurgical, leaching, solvent extraction/stripping, chemical precipitation, and others. The process steps can be combined in different ways, depending on factors like quantity and characteristics of the available materials, and quantity and value of the materials that can be recovered.[27]

An overview of the battery recycling process pathways is provided in Figure 2. The process can be broken down into a few major steps, including physical separation where batteries are shredded and separated by size, leading to a pyrometallurgical step to reduce the overall volume of material and leave behind only metals, which can be recovered either through a direct recycling or hydrometallurgical step.

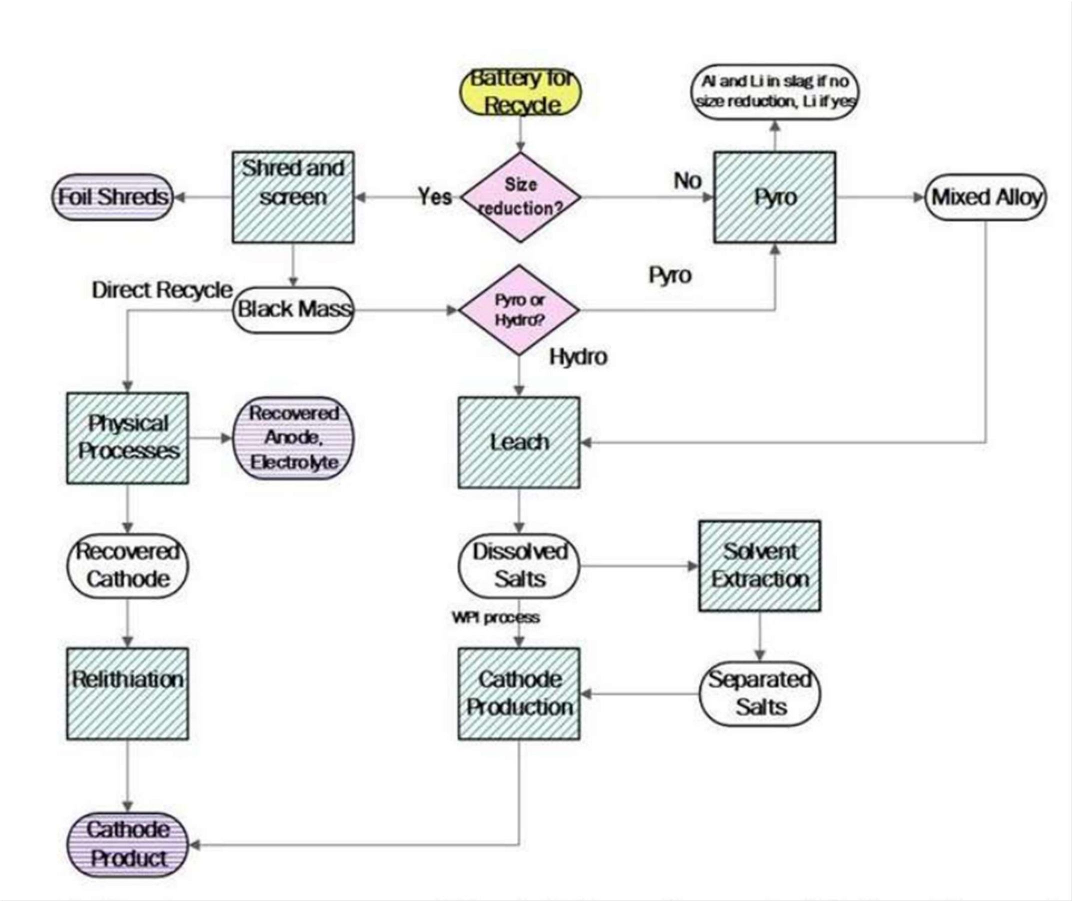

Figure 2. An overview of the possible lithium-ion battery recycling pathways.(27)

The primary hydrometallurgical processes are acid or alkaline leaching, chemical precipitation, separation, and electrochemical recovery.(21-24) Recently, research has focused on solvent extraction methods as a more environmentally friendly and economical way to recover high purity metals.(26) Adding hydrometallurgical processes often combine solvent extraction and stripping with acid leaching, pH neutralization, separation, and thermal evaporation, with the goal of removing impurities and selectively extracting pure battery grade materials. The complexity of the process steps, particularly hydrometallurgical processes that are sensitive to many operating variables (pH, temperature, composition, etc.) highlights the need for computer-assisted battery recycling process models. Some hydrometallurgical unit operations display inherent problems such as slow kinetics, inefficient solid-liquid separation, high cost, and low purity(25) which further necessitates the use of mathematical models to predict these non-equilibrium conditions.

THE IMPORTANCE OF MODELING AND SIMULATION

Solvent extraction modeling is challenging for computational models because of the complex chemical behavior in LLE systems, the presence of multiple chemistries and contaminants, and the possible nonideal behavior. Models must account for chemical, physical, and thermodynamic principles in multiphase multicomponent systems, with non-standard feed compositions seen in battery recycling processes. The nonlinear nature of these relationships and the presence of azeotropes or miscibility gaps complicate modeling efforts. Chemical speciation plays a primary role in extraction efficiency, and can be influenced by pH, ionic strength, and the presence of complexing agents. Interfacial phenomena like mass transfer limitations, mixing, emulsions, and kinetics also play a significant role in extraction efficiency, but are beyond the scope of this modeling effort. While modeling these complex behaviors is not a simple task, it highlights the importance of computational methods for process optimization, which analyze the effects of numerous competing variables.

The ability to accurately model the chemical behavior is critical to process design and scale-up. Translating complex processes to industrial scale requires models that can accurately predict performance over a wide range of operating conditions. This involves not just chemical and physical modeling but also considerations of engineering principles, equipment design, safety, and environmental impact.

SIMULATION APPROACH AND ANALYSIS

A process simulation was developed for the extraction of cobalt and lithium from a lithium cobalt oxide (LCO) cathode. The validated SX database was used to test and optimize the operating conditions of a standard hydrometallurgical process. The hydrometallurgical portion of the LCO recycling process is modeled based on feed composition and cobalt extraction steps described in (26) and it is combined with a lithium extraction process described in (28). The feed composition is 24,880 mg/L Co, 3000 mg/L Li, 37.94 mg/L Ni, 159.5 mg/L Fe, 16.06 mg/L Mn, 782.7 mg/L Cu, 1800 mg/L Al, 13 mg/L Ca, 37.6 mg/L Na.

The process model can be split into two sections: cobalt recovery and lithium recovery. The cobalt recovery section is outlined in Figure 3 and consists of impurity removal through pH neutralization with a sodium hydroxide/sodium carbonate mixture. Next, the cobalt-containing stream enters the solvent extraction process with 50% saponified 0.5M Cyanex 272 in kerosene. The solvent is then stripped with 2M H2SO4, and the resulting cobalt sulfate product is precipitated via an evaporation/crystallization unit.

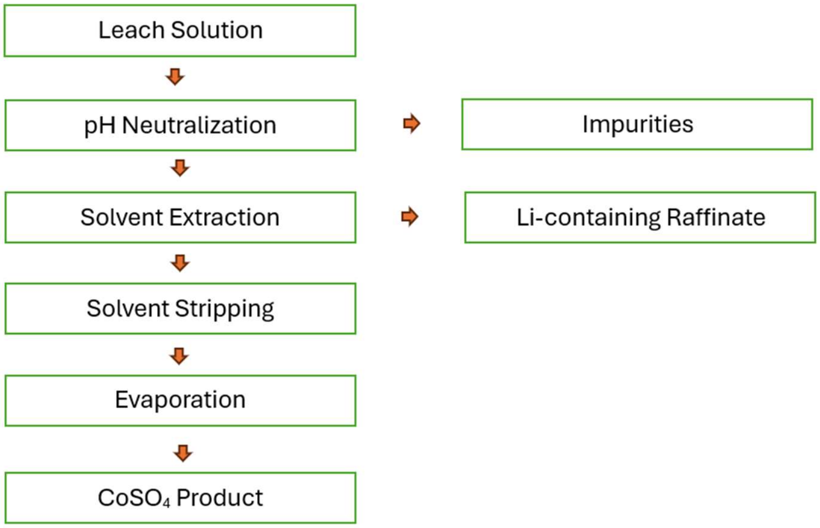

Figure 3. Overview of the hydrometallurgical process modeled for the cobalt extraction step using Cyanex 272.

The lithium extraction section is shown in Figure 4. Using the raffinate from the cobalt extraction process, the lithium-containing stream is acidified with HCl prior to solvent extraction with 0.06M D2EHPA in kerosene. The organic phase is then stripped using 2M H_2SO_4. Finally, a lithium carbonate product is produced via pH neutralization with lime, carbonation with sodium carbonate, and deionized water washing.

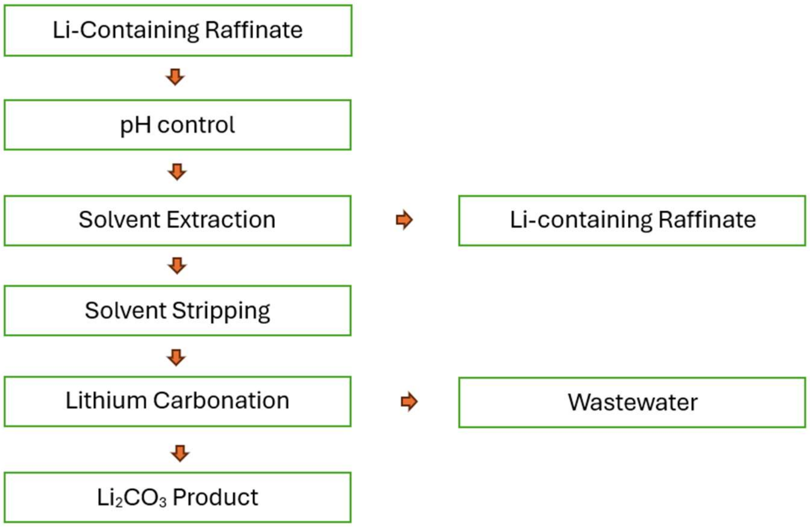

Figure 4. Overview of the hydrometallurgical process modeled for the lithium extraction step using D2EHPA.

The process was modeled using an equilibrium-based steady state flow sheeting software tool where solvent extraction, solvent stripping, and evaporation process units were each modeled as single theoretical equilibrium stages. Figure 5 depicts how the process simulation was designed using a combination of mixers and three- and two-phase separators.

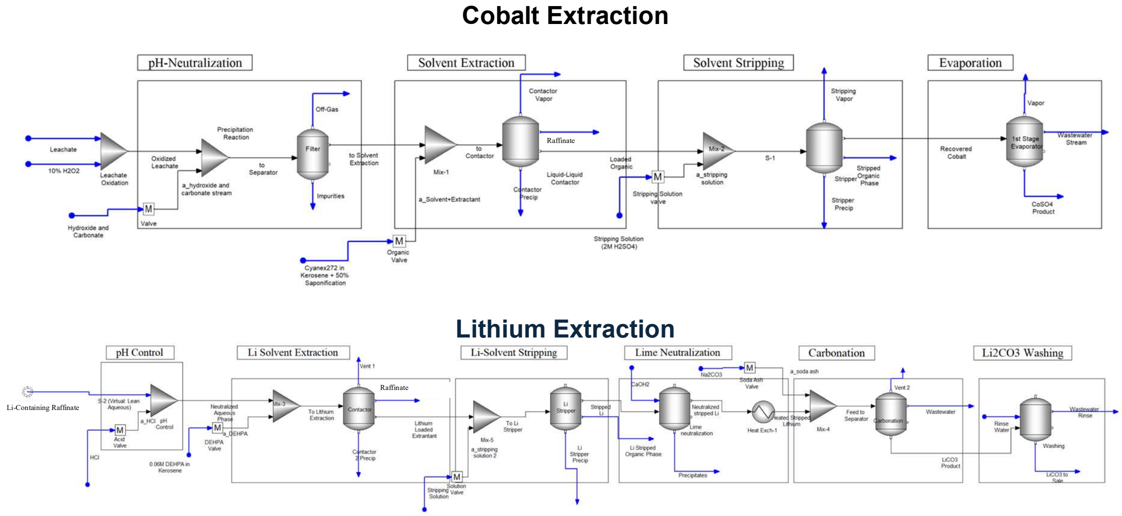

Figure 5. The developed process model for the two solvent extraction steps. The first step uses Cyanex 272 to extract Cobalt from a LCO cathode leach solution, and the second step extracts lithium from cobalt-lean aqueous phase using D2EHPA.

RESULTS

The solvent extraction process units were optimized by adjusting operating pH, solvent-to-feed ratio, and operating temperature. The operating temperature sensitivity was evaluated but it was ultimately determined that the natural rise in process fluid temperature due to heats of reaction at the neutralization step were sufficient for the SX performance while serving the additional purpose of eliminating the need for external heat sources.

Ionic flowrates for the primary process streams in the cobalt extraction and the subsequent lithium extraction processes are reported in Table 1 and 2. The composition results show how cobalt, nickel, lithium, and impurities move through the battery recycling process. The primary contributor to product recovery is solvent extraction and stripping. Product purity is driven by the upstream neutralization and precipitation steps responsible for pH adjustment and impurity removal prior to product precipitation. A benefit to using an advanced electrolyte thermodynamic model like this is the capability to couple pH-driven process units with the solvent extraction steps.

Table 1. Cobalt extraction process with Cyanex 272 showing key ion composition for primary process steps.

	Leachate Liquor	Impurity Precipitation	to Solvent Extraction	After Solvent Extraction	Recovered Cobalt	Li-Containing Raffinate
	mol/hr	mol/hr	mol/hr	mol/hr	mol/hr	mol/hr
Al(+3)	66.71	66.71	0	0	0	0
Ca(+2)	0.32	731.581	19.46	0.96	0.16	5.34
Co(+2)	422.17	0	422.17	415.40	411.08	0.26
Cu(+2)	12.32	12.28	0.03	0	0	0.01
Fe(+2)	2.86	2.84	0.01	0	0	0
Li(+1)	432.22	0	432.22	0	0	432.22
Mn(+2)	0.29	0.15	0.15	0	0	0.03
Ni(+2)	0.65	0	0.65	0.65	0	0

1. Calcium is added to the process as $CaCO_3$ to induce chemical precipitation of impurities prior to solvent extraction.

Table 2. Lithium extraction process with D2EHPA showing key ion composition for primary process steps.

	Li-Containing Raffinate	Post SX (feed to carbonation)	Precipitation from Lime Softening	Raffinate	Wastewater	$LiCO_3$ to Sale
	mol/hr	mol/hr	mol/hr	mol/hr	mol/hr	mol/hr
Al(+3)	0	0	0	0	0	0
Ca(+2)	5.34	4.34	260.51[1]	0.083	0.027	3.93
Co(+2)	0.26	0.00035	0.26	0.00000	0.000090	0.00018
Cu(+2)	0.0051	0	0	0.0045	0	0.00047
Fe(+2)	0.0021	0.000020	0	0.0021	0.000020	0
Li(+1)	432.22	301.10	0	0.00025	118.50	300.79
Mn(+2)	0.026	0	0.00055	0.025	0	0

1. Calcium is added to the process as $Ca(OH)_2$ to neutralize the process stream prior to $LiCO_3$ of impurities prior to solvent extraction.

For the cobalt extraction process, the optimized conditions were a feed stream pH of 6.2, A/O ratio of 1:4, and process operating temperature of 36°C. Together, these conditions generate a final Co recovery of 97.3 % and $CoSO_4$.1H2O purity of 99.9%. These results are consistent with the lab experiment findings in (26) although the lower A/O ratio compared to literature indicates opportunity for further model optimization. In the lithium extraction process, the ideal operating conditions were found to be pH 1.5, A/O (molar) ratio of 1:2 and operating temperature of 27°C giving a final recovery of 69.5% and 98.7% purity. Similarly, these operating conditions are consistent with experimental findings on D2EHPA extraction of lithium(28). But like with cobalt extraction, the lower A/O ratio in the model compared to literature indicates further opportunity for model optimization like adding additional separation stages and recycling raffinate and extractant streams.

CONCLUSIONS AND FUTURE WORK

A new database for solvent extraction has been introduced and integrated with the MSE thermodynamic framework to effectively model the solvent extraction process for the recovery of Co, Ni, and Li with D2EHPA and Cyanex 272 extractants. The models can be used in a process simulation tool to assist in optimization and scaleup of hydrometallurgical processes found in battery recycling. In the future, the SX database will be expanded to include additional high priority materials like rare earth elements, manganese, copper, and corresponding contaminants. The aim will be to develop a generalized model that encompasses solvent extraction in multicomponent systems representative of battery recycling. Additionally, solvents and diluents will be incorporated as data becomes available.

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