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DEVELOPMENT OF AN ENVIRONMENTALLY FRIENDLY LITHIUM ION BATTERY (LIB) RECYCLING PROCESS

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KEY FINDINGS

The main aim of this work was to evaluate the technical feasibility of using organic acids as lixiviants for Co, Li and Ni recovery from end-of-life lithium-ion batteries (LIBs) and to recover the metals from the resulting pregnant leach solution (PLS). Batch leaching tests to investigate the effects of H_2O_2 addition, temperature and acid concentration on metal dissolution were performed using citric acid and DL-malic acid. Leaching results suggest that organic acids can possibly substitute inorganic acids as environmentally friendly lixiviants. Following leaching solvent extraction and precipitation tests were performed for metal recovery from the pregnant leach solutions. The proposed process involves Mn and Al extraction from PLS using D2EHPA, followed by phosphate precipitation at 50℃ targeting Co and Ni and subsequent phosphate precipitation at 80℃ for Li recovery. The process yields three products: a 93% pure Mn product, a Co-Ni product with 42 wt. % Co and 57 wt. % Ni and a Li product with 89 wt. % Li. The results highlighted key fundamental and technical aspects of the Li-Co-Ni-Mn recovery process that require further investigation especially in challenging recovery-cost paradigm with solvent extraction and precipitation processes.

INTRODUCTION

In general spent LIBs are discarded as domestic waste, which is environmentally unacceptable. According to the directives published in many countries, adequate disposal of spent batteries may involve landfilling, stabilization, incineration or recycling. In landfills, heavy metals have the potential to leach slowly into soil, groundwater or surface water. The heavy metals contained in spent LIBs such as Co, Li, Fe and Cu accumulate in the environment and metal oxides will be converted into their metallic forms during the incineration of garbage and may result in water pollution. Additionally, safe disposal in landfills or the stabilization of battery residues have become more expensive because of the increasing amounts of waste produced and because of the limited storage capacity of sanitary landfills and special waste dumpsites.

The recovery of metals from spent LIB components is therefore beneficial not only for environmental protection, but also for the provision of expensive raw materials such as cobalt, nickel and lithium. The main steps in hydrometallurgical process routes used for LIBs recycling are dismantling, size reduction, physical separation and leaching. Solvent extraction and ion exchange are used for the recovery and separation of metal values from solution and electrometallurgy or chemical precipitation is used for converting them into a saleable form. In recent years, research has shifted towards the use of more environmentally friendly lixiviants in leaching valuable metals from lithium ion batteries. The objective of this project was to evaluate the technical feasibility of using organic acids, which potentially are less harmful to the environment than mineral acids, as lixiviants to recover lithium, cobalt and nickel from LIBs. A conceptual flow sheet incorporates leaching with citric acid, Mn and Al extraction with D2EHPA from PLS after leaching, followed by phosphate precipitation at 50℃ and subsequent phosphate precipitation at 80℃. This results in three valuable product streams, a Co-Ni product with composition: 0.24 wt. % Al, 42 wt. % Co, 0.11 wt. % Cu, 0.51 wt. % Li, 0.2 wt. % Mn and 57 wt. % Ni, an 89% pure Li product with composition: 0.01 wt. % Al, 6 wt. % Co, 0.3 wt. % Cu, 0.2 wt. % Mn and 4 wt. % Ni and a 93% pure Mn solution. The project has led to significant capacity development in the research field related to LIBs recycling from end-of-life lithium ion batteries.

APPROACH

Based on a literature review of existing processes and unit operations, a conceptual flow sheet for Li-Co-Ni-Mn recovery from LIBs was proposed (Figure 1). Bench-scale tests were performed to evaluate the effect of key process variables in the process and the performance of the respective key unit operations, namely leaching, solvent extraction, and precipitation.

Leaching

EoL LIBs were obtained from a facility in South Africa. Using 1.5M citric acid with 2% v/v H_2O_2 at 95℃ and 20 g/L pulp density, 95% Co, 96% Li and 99% Ni were recovered after 30 minutes. With 1M DL-Malic acid in the presence of 2% v/v H_2O_2 at 95℃ and 20 g/L pulp density, 99% Co, 96% Li and 99% Ni were recovered within 30 minutes.

Solvent extraction

Solvent extraction tests showed that separation of Mn and Al from a Co, Li and Ni citrate solution was possible. Using 10% v/v D2EHPA at pH 2.5, O/A ratio 5 and room temperature, 47% Al, 7% Co, 9% Li, 94% Mn and 3% Ni were extracted in one stage. The McCabe-Thiele method determined that two equilibrium stages are required to extract over 99% Mn. This was verified experimentally and 99% Mn and 89% Al were extracted, with 13% Co, 17% Li and 6% Ni co-extraction in two stages.

Precipitation

Phosphate precipitation tests revealed that the solubility of Li_3PO_4 decreases with an increase in temperature. When the temperature was varied from 50°C to 80°C, precipitation of Li as Li_3PO_4 increased from around 3% to 72%. However, solubility of the rest of the metal phosphates appeared not to be affected by temperature as there was consistent phosphate precipitation from 50°C to 80°C. It was therefore concluded that Li can be separated from the rest of the elements in two phosphate precipitation stages. The first stage at 50°C which targets all the metals except Li, followed by the second one at 80°C which targets Li.

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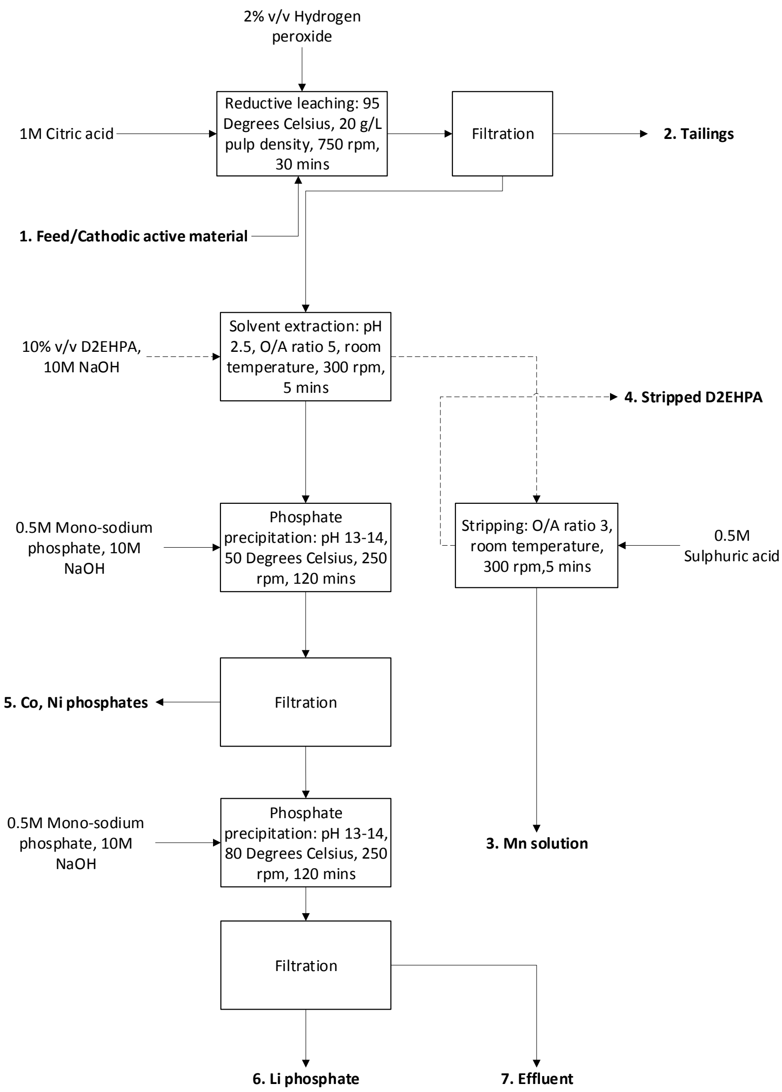

Figure 1. Conceptual flow sheet for Li, Co, Ni, Mn recovery from end-of-life lithium-ion batteries (LIBs)

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