RECENT TECHNOLOGICAL PROGRESS IN METALS' RECOVERY FROM SPENT NCM BATTERY PROMOTED BY NEW SEPARATION REAGENTS

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ABSTRACT

Valuable metals recovery from the spent lithium batteries (black mass) is of vital importance, since it eliminates the heavy metal pollution threat and provides an alternative solution for the supply crisis of critical metals (Ni/Co/Mn). However, traditional recovery technologies that consisted of leaching and individual element separation by solvent extraction still faced several challenges: separation difficulties between Ni^{2+}(Co^{2+})/Mg^{2+}, Mn^{2+}/Ca^{2+}, Li^{+}/Ni^{2+}, Li^{+}/Na^{+}(K^{+}) and incomplete removal of fluorine due to the limited separation coefficient of previous methods. To solve these issues, a series of solvent including HBL-120 for Ca extraction from Mn, HBL-116 for Ni(Co) extraction from Mg and Li, HBL-121 for Li extraction from Na(K), and HBL-221 for F extraction from Ni(Co&Mn) were designed and synthesised.

(1) Ca separation from Mn with HBL-120 makes the preferential removal of Ca before impurities extraction with D2EHPA is possible, which eliminates $CaSO_4$ scaling issue during stripping of impurities extraction with D2EHPA and directly produces pure $MnSO_4$ product.

(2) Selective Ni(Co) extraction from Mg containing solutions shortens the Co extraction (HEHEHP) - Ni extraction (HEHEHP) - Mg extraction (Cyanex 272) into Ni(Co) extraction (HBL-116)-Mg precipitation, which saves >50% of labour and land.

(3) Fluorine originating from the electrolyte and adhesive cannot be completely removed via traditional methods and brought massive Ni(Co) loses in fluorine removal residue. Specific extractant HBL-221 binds fluorine and extracted Me-F complex into organic phase, with <5mg/L F left in raffinate and <0.1 Ni(Co&Mn) loss.

(4) Li generally reports into a concentrated Na_2SO_4 solution since all the extraction processes for Ni/Co/impurities adopted Na-saponification. However, traditional carbonate precipitation – evaporating concentration process recovered only ~85% of Li (~10% Li loss in Na_2SO_4 crystal) and produced crude Li_2CO_3 entrained considerable Na_2SO_4. Selective Li extraction from Na(K) concentrated solutions with HBL-121 significantly elevated the Li recovery to >99% and produced Li_2SO_4 solution with Li/Na(K)>100.

So far, all technologies mentioned above have been applied individually or packaged in many hydrometallurgical plants for spent LIBs recycling in China and USA (pilot test). Based on these new extractants, an alternative short process for metal recovery from the leaching solutions of NCM black mass was proposed which includes Ca(Zn) extraction with HBL-120, impurities extraction with D2EHPA, fluorine extraction with HBL-221 (if needed), Co extraction with HEHEHP, Ni extraction with HBL-116 (or Ni/Co co-extraction with HBL-116), Mg precipitation with NaOH, Li extraction with HBL-121. This process owns merits of high metal recovery, reagent saving, short process, and economy.

Keywords: Spent LIBs, recovery, selective extraction, separation, fluorine removal.

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