

Hydrometallurgical Treatment for Mixed Waste Battery Materials

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Abstract. Hydrometallurgical experiments are generally required to assess the appropriate treatment process before the establishment of the industrial recovery process for waste battery materials. The effects of acid systems and oxidants in metal leaching were studied. The comprehensive leaching effects of the citric acid were superior to the sulfuric acid. The potassium permanganate inhibits the dissolution of metals. Thermodynamic calculations showed that metals precipitate more easily in sulfuric acid system than in citric acid system. The Fe precipitation efficiency in sulfuric acid system was 90% at pH 3.5, but with considerable losses of Co (30%) and Ni (40%). The proper pH and organic/aqueous (O/A) ratio for Fe and Zn removal with Di-(2-ethylhexyl) phosphoric acid extraction were 2 and 0.5, respectively; while for the removal of Cu and Mn, the best pH and O/A ratio were 3 and 0.75, respectively. Crude manganese carbonate and a cobalt-nickel enriched liquid were obtained by selective precipitation in raffinate using an ammonium bicarbonate solution. In citric acid systems, the precipitation efficiency of Co, Ni, Mn, Fe, Cu and Zn were less than 20% at pH 7. The proper pH and O/A ratio for the separation of the metals in two groups (Ni/Co/Cu and Mn/Fe/Zn) were 1.5 and 2. The cobalt-nickel-copper enriched liquid was finally obtained.

1. Introduction

Recovery of metals such as cobalt, nickel and manganese from secondary resources has been an important area of "urban minerals" exploitation. Cobalt and nickel secondary resources usually include spent lithium-ion batteries, nickel-metal hydride battery waste, metal scraps, complex mineral wastes and smelting slags [1]. Hydrometallurgical experiments for waste materials are often required to roughly acquire the treatment process before the establishment of any industrial recovery process. The recovery process often contains these steps: acidic leaching, metal separation and product synthesis. Due to the complex and diverse composition of secondary resources, the leaching methods are different. Sulfuric acid is commonly used in the leaching of spent batteries, and the extraction ratio of Co can achieve at least 70% [2]. In addition, some organic acids such as citric acid ($C_6H_8O_7$), malic acid ($C_4H_5O_6$), glycine, EDTA and DTPA, also were used to leach or extract metals of spent batteries or waste catalysts [3,4]. The leaching efficiency of major metals for these organic acids can also reach more than 70%. Apart from leaching agent, the oxidant is a key factor in promoting the dissolution of valuable metals during leach process. The use of hydrogen peroxide as an oxidizing agent can promote leaching of nickel, cobalt and rare earth from waste capacitors and batteries [5]. The use of potassium permanganate or hydrogen peroxide oxidation during acid leaching of indium sulfide minerals can significantly reduce the apparent activation energy and reaction order, increasing the reaction rate [6]. Potassium permanganate can also play the role of Mn remover [7]. Different leaching systems will



affect the subsequent separation and recovery of metals. Theoretical studies have shown that the metal separation behaviors are different in different solution systems of Me-OH^- , $\text{Me-OH}^--\text{CO}_3^{2-}$, $\text{Me-OH}^- \text{S}^{2-}$, $\text{Me-OH}^- \text{NH}_3$ and $\text{Me-OH}^- \text{NH}_3\text{-CO}_3^{2-}$ [8]. Applying different solution system different metals can be selectively precipitated. According to thermodynamic calculations, the $\text{Me-OH}^- \text{NH}_3\text{-CO}_3^{2-}$ solution system can remove Fe efficiently with a low cobalt and nickel loss, and the iron precipitate showed a good filtration performance [9]. Mo and Al can be effectively separated from waste Ni-Mo catalysts in EDTA leaching system using a selective precipitation method, and $\text{Ni}_3(\text{PO}_4)_2$ was recovered by ion salt replacement method with a purity over 96% [10]. According to these results, theoretical and experimental studies on metal separation are effective and feasible for the comprehensive recovery of metals from secondary resources.

In this paper, waste battery material was used as raw materials. Sulfuric and citric acids with an oxidizing agent were used to leach the waste battery material to obtain the metal solution. Thermodynamic calculations were performed for the two leaching systems to study the metal separation behavior. Solvent extraction was then used to further separate the metals, and the metal pregnant liquor or metal compound was finally obtained.

2. Experimental

2.1. Leaching

Waste battery material obtained from a recycling company (GEM High-Tech Co., Ltd., China) was crushed and screened. Powders with a particle size of 200 mesh were leached with agitation of 800 rpm at 85 °C for 2 hours, at a liquid to solid ratio (L/S) of 40:1, in four leaching systems: (1) 2.5 mol/L sulfuric acid + 5 vol% hydrogen peroxide (H_2O_2), (2) 2.5 mol/L citric acid + 5 vol% H_2O_2 , (3) 2.5 mol/L sulfuric acid + 5 vol% H_2O_2 + 20 wt% potassium permanganate (KMnO_4), and (4) 2.5 mol/L citric acid + 5 vol% H_2O_2 + 20 wt% KMnO_4 . After leaching, the metal leaching efficiency (L) was calculated according to formula (1):

$$L = \frac{M \times C_0 \times V_0}{m \times w\%} \times 100\% \quad (1)$$

where M and C_0 are the molecular mass and concentrations of metal ions in the leach liquor, respectively; V_0 is the leach liquor volume; m is the mass of cobalt-bearing waste and $w\%$ is the metal mass fraction.

2.2. Precipitation

The metals were precipitated from the leach solutions and the solutions were filtered at different pH values (3-7). The metal precipitation efficiency (P) was calculated according to formula (2):

$$P = \left(\frac{C_0 V_0 - C_1 V_1}{C_0 V_0} \right) \times 100\% \quad (2)$$

where C_0 and C_1 are the metal ion concentrations in the solution before and after precipitation; V_0 and V_1 are the solution volumes before and after precipitation.

2.3. Solvent Extraction

Di-(2-ethylhexyl) phosphoric acid (D2EHPA or P204) was used to further extract metals from the sulfuric and citric acid systems at 25 °C, with a P204 concentration of 30% and a saponification ratio of 65%. Organic/aqueous (O/A) phase volume ratios of 0.25-2.5 and pH values of 1.0-3.0 were investigated. The metal ion extraction efficiency (E) was calculated according to formula (3):

$$E = \frac{C_1 V_1 - C_2 V_2}{C_1 V_1} \times 100\% \quad (3)$$

where C_1 and C_2 are the metal concentrations in the aqueous phase before and after the extraction; V_1 and V_2 are the aqueous phase volumes before and after the extraction.

2.4. Analysis

The waste battery material composition was analyzed by x-ray fluorescence (XRF-1800, Shimadzu, Japan). The metal concentration of the leachate, the filtrate and the affinate were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 7000DV, PerkinElmer, U.S.A.). The structure of the raw material and the product were investigated by x-ray diffraction (XRD, 7000 S/L, Rigaku, Japan).

3. Results and discussion

3.1. Material Characterization

The composition and the structure of the waste battery material were studied by XRF and XRD (shown in Fig. 1). The main components of the waste material are Co (0.24 wt.%), Ni (1.01 wt.%), Mn (35.22 wt.%), Zn (21.86 wt.%), Fe (3.64 wt.%) and Cu (0.12 wt.%). The main phases of the waste battery material are $(\text{Co,Mn})(\text{Co,Mn})_2\text{O}_4$, $\text{Co}_{1.29}\text{Ni}_{1.71}\text{O}_4$, ZnO , $\text{Cu}_{0.95}\text{Co}_{2.05}\text{O}_4$ and FeMnO_3 , suggesting that this waste is a complex mixture of cobalt-nickel batteries and zinc-manganese batteries.

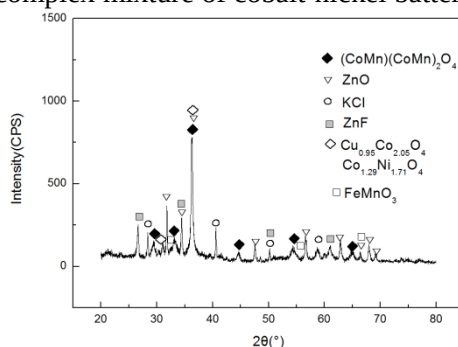


Fig. 1 Mixed waste battery material XRD analysis

3.2. Leaching

The leaching efficiency of metals in sulfuric acid-hydrogen peroxide system is shown in Fig. 2(a). Most of the metals can be leached thoroughly. The leaching efficiency of Ni and Mn are almost 100%, the Co leaching efficiency is 82.9%, and the Fe, Cu and Zn leaching efficiencies are over 70%, indicating that the waste metals can be easily dissolved in a strong acidic environment with hydrogen peroxide as oxidant.

The leaching efficiency of metals in citric acid-hydrogen peroxide system is shown in Fig. 2(b). The metals exhibit different leaching behaviors. The Ni leaching efficiency is almost 100%, the Co leaching efficiency is 85.1%, and the Fe, Cu and Zn leaching efficiencies are over 50%. The Mn leaching efficiency displays the lowest value (28.3%). The organic acidic environment with hydrogen peroxide as oxidant favors valuable metals dissolution (Co and Ni) but does not promote the dissolution of Mn, Fe, Zn and the other metals. The citric acid system is beneficial for the selective dissolution of metals in the mixed battery waste as compared to the sulfuric acid system.

As the Mn content in the mixed waste battery material increases, the addition of H_2O_2 and KMnO_4 for Mn removal during the leaching process can reduce subsequent purification difficulty. The H_2SO_4 - H_2O_2 - KMnO_4 leaching results are shown in Fig. 2(c). The leaching efficiency of Mn, Fe, Zn, etc. are all below 42%, and the leaching efficiency of Mn is only 10.3%. Meanwhile, the leaching efficiency of both Co and Ni decrease to 32.9% and 69.8%, respectively, as compared to the systems without H_2O_2 - KMnO_4 . The metal dissolution behavior will be changed by adjusting the oxidant apart from changing the leaching agent.

The leaching efficiency of metals in citric acid-H₂O₂-KMnO₄ system are shown in Fig. 2(d). The metal dissolution behaviors are similar to that in H₂SO₄-H₂O₂-KMnO₄ system. Since the organic acid and the KMnO₄ do not encourage the dissolution of the related metals, the leaching efficiency of the metals is further reduced as compared with the H₂SO₄-H₂O₂-KMnO₄ system. The leaching efficiency of Mn, Fe and other metal is dropped to less than 20%, but the leaching efficiency of the valuable metals, Ni and Co, are also very low, only 23.1% and 48.2%, respectively, which is unfavorable for the recovery of Ni and Co.

Based on the above results, the citric acid is better than the sulfuric acid because the first favors the leaching of Co and Ni but is not conducive to the dissolution of the other metals. Using KMnO₄ as an oxidant, the Mn leaching efficiency can be significantly reduced but the dissolution of the other metals also decreases. Therefore, the citric acid-H₂O₂ system is the best leaching system for the mixed waste battery material used in this study.

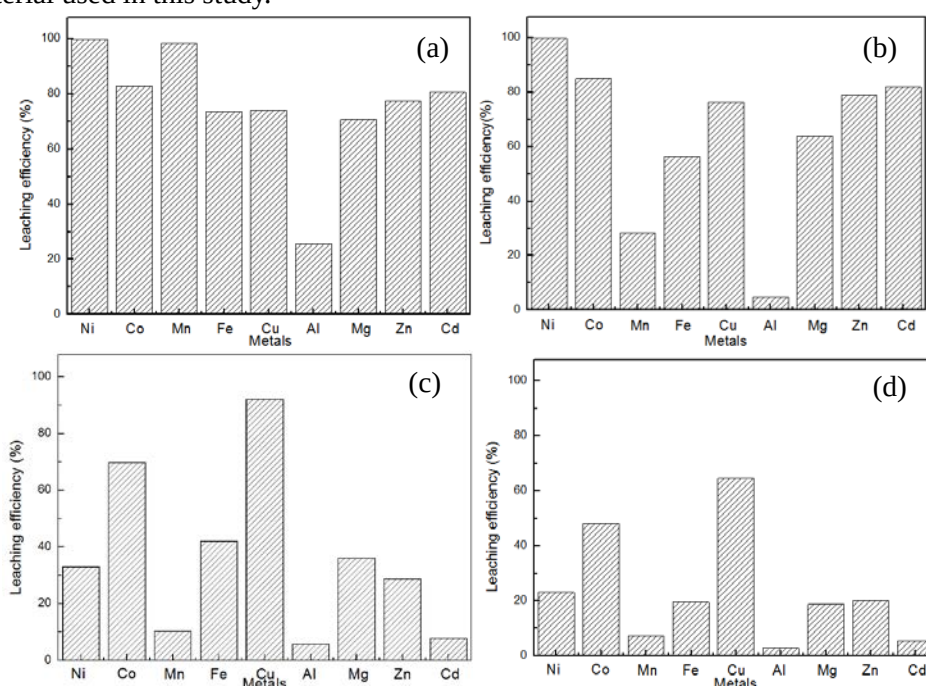


Fig. 2 Metal leaching efficiency in (a)H₂SO₄-H₂O₂; (b) H₃Cit-H₂O₂;
 (c) H₂SO₄-H₂O₂-KMnO₄; (d) H₃Cit-H₂O₂-KMnO₄

3.3. Precipitate

3.3.1. Theoretical Analysis According to the thermodynamic data from Ref. [11], the metal precipitation trends can be predicted by thermodynamic calculation. The relationships between the logarithm of metal ion concentration ([Me]) and pH in the sulfuric acid system and the citric acid system are shown in Fig.3. As can be seen from Fig. 3(a), the metal concentration decreases with an increase of pH up to the value of 9.5; i.e., theoretically, all of the metals achieve the maximum precipitation at pH 9.5. In sulfuric acid system, Fe precipitates completely at pH 3 and can be separated from the other metals; Cu precipitates and can be separated from the other metals at pH 5.5-6.5, accompanied by some loss of cobalt; most metals precipitate completely at pH>7. As can be seen from Fig. 3(b), the concentration of each metal also decreases with an increase of pH in the citric acid system, but the decline is not as pronounced as compared with the sulfuric acid system. Theoretically, in the citric acid system, Fe precipitates completely at pH>7, while the concentrations of Co and Ni remain stable, and do not precipitate completely at pH 6-12, indicating that these metals are much easier to precipitate in the sulfuric acid system than in the citric acid system.

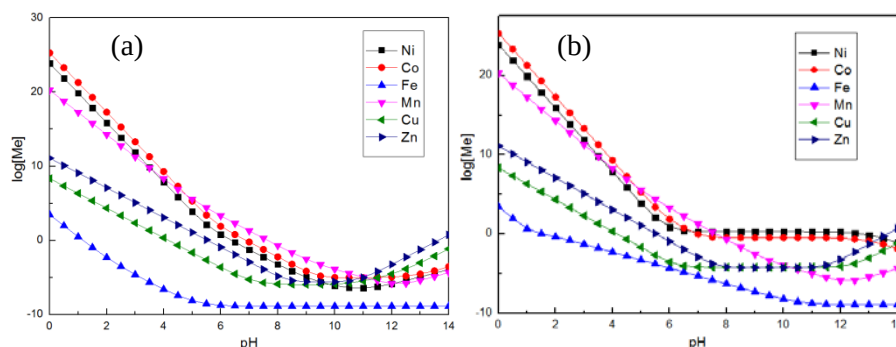


Fig. 3 Theoretical log[Me]-pH curve in (a) sulfuric acid system; (b) citric acid system

3.3.2. Experimental Study Fig. 4(a) shows the experimental metal precipitation efficiencies in sulfuric acid leaching solution at different pH values. The precipitation efficiency of each metal increases with pH, which is consistent with the theoretical prediction. The Fe precipitation efficiency is 90% at pH 3.5. Since the content of Co and Ni are relatively low in the mixed waste battery material, the low precipitation efficiency of 30% for Co and 40% for Ni will result in a great loss of these valuable metals; therefore, a lower pH is recommended for Fe pre-removal, followed by the removal of most impurities by extraction. Other studies have shown that Fe^{3+} and Cu^{2+} can be pre-precipitated with a pH adjustment to 5.5 [12], but for this material with low Co and Ni contents it is not suitable. As Mn, Cu and Fe can be removed by P204 extraction in the next stage, a extraction after leaching is also feasible. Fig. 4(b) shows the experimental metal precipitation efficiencies in citric acid leaching solution under different pH conditions. The precipitation efficiency of all the metals increase gradually with pH. At pH 5, the precipitation efficiency of Ni, Co, Fe, Mn, Cu and Zn is 11.5%, 12.7%, 16.3%, 12.5%, 15.4% and 14.4%, respectively, and at pH 7 their precipitation efficiencies are still less than 20%. As can be seen, metals separation is difficult in the citric acid system, which is consistent with the theoretical prediction; therefore, a metal separation using direct extraction should be considered.

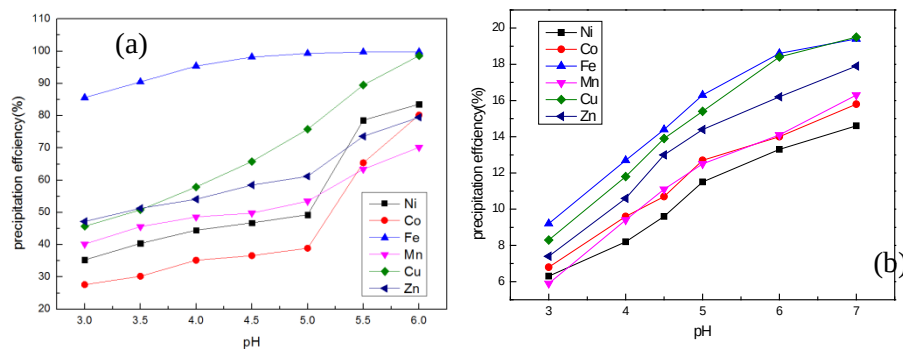


Fig. 4 Metal precipitation efficiencies at different pH (a) in sulfuric acid system; (b) in citric acid system

3.4. Extraction

Fig. 5(a) shows the effect of pH on the extraction efficiency of different metal ions in sulfuric acid system. The metal extraction efficiency increases with pH. The extraction order according to pH values from low to high is Fe, Zn, Mn, Cu, Co and Ni, but the extraction efficiency of Fe always remains over 80% while the Zn extraction efficiency increases to 93% at pH 2. The extraction efficiency of the other metals are lower than 16%. For the removal of Fe and Zn, the suitable pH is 2, but for the removal of Cu and Mn the best pH is 3. Fig. 5(b) shows the effect of O/A ratios on the extraction efficiency of different metal ions in sulfuric acid system. The metal extraction efficiency increases with O/A ratio. Lower O/A ratios generally mean a fewer organic phase compared to a certain amount of aqueous phase and a limited extraction capacity. When the O/A ratio is low, metal ions such as Mn, Fe, Cu, etc., with a strong affinity to P204, can enter into the P204 organic phase

preferentially and be separated from Co and Ni. When the O/A ratio reaches a certain level, the metals with a weak affinity to P204 also entered into the organic phase, and there is no separation effect among the metals. According to Fig. 11, the extraction efficiency of Fe and Zn are high while the extraction efficiency of the other metals are still low at an O/A ratio of 0.5, so 0.5 is the suitable O/A ratio for Fe and Zn separation, while 0.75 is the proper O/A ratio for Cu and Mn separation.

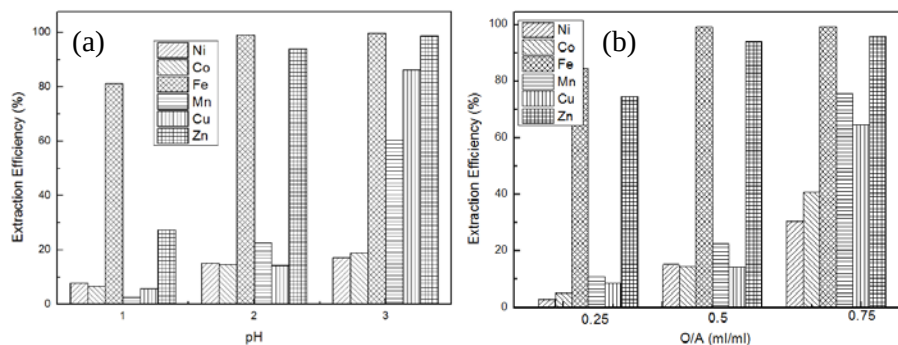


Fig. 5 Extraction efficiency of metals in sulfuric acid system (a) effect of pH; (b) effect of O/A ratio

Fig. 6(a) shows the effect of pH on the extraction efficiency of different metals in citric acid system. In this system, the extraction efficiency of all the metals increased slowly as the pH increased. Since the extraction ability of P204 is very sensitive to pH and metal ion valence, and the citric acid is a ternary weak acid, which will release H^+ step by step to stabilize the pH of the solution, it is not beneficial for the metal extraction reaction. It is apparent from Fig. 12 a segregation effect between the Ni/Co/Cu group and the Mn/Fe/Zn group. The proper pH is 1.5 where the extraction efficiency of Ni, Co, Cu, Mn, Fe, Zn is 15.8%, 16.3%, 22.4%, 80.2%, 64.8% and 76.8%, respectively; however, the separation effect among Ni, Co, Cu, or Mn, Fe, Zn are very poor. Fig. 6(b) shows the O/A ratio effect on the extraction efficiency of different metal ions in citric acid system. Similar to the sulfuric acid system, the extraction efficiency of each metal increases with O/A ratio, but with a smaller degree as compared with the sulfuric acid system, indicating that more organic phase is needed in the extraction process. This could be due to the formation of metal complexes in the citric acid system, which is difficult to extract. In addition, the excess citric acid can combine with the extractant, requiring more P204. The extraction efficiency of Mn, Fe and Zn are relatively high and the extraction efficiency of Ni, Co and Cu are relatively low at O/A ratio of 2.0, indicating a relatively good separation effect.

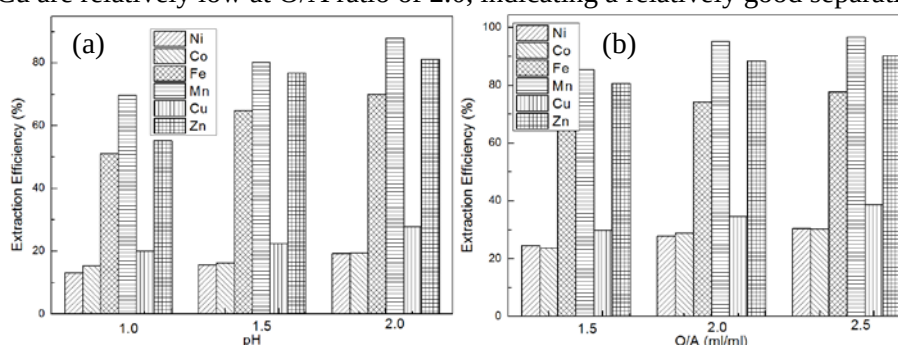


Fig. 6 Extraction efficiency of metals in citric acid system (a) effect of pH; (b) effect of O/A ratio

3.5. Recovery

Based on the theoretical and experimental leaching results obtained for the mixed waste battery material in sulfuric and citric acid systems, it is believed that the metal separation in the citric acid system is not as good as in the sulfuric acid system due to complexing effect. Finally, only Co-Ni-Cu-enriched liquid was obtained after solvent extraction in the citric acid system, and Co-Ni-enriched

liquid and crude manganese carbonate (Fig. 14) were obtained after selective precipitation by ammonium carbonate solution.

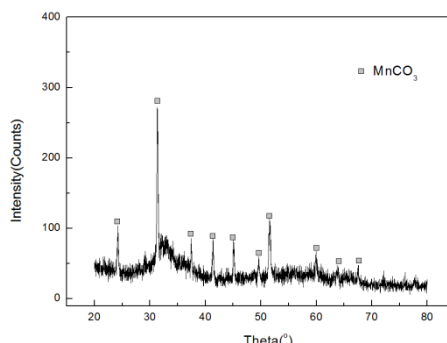


Fig. 14 XRD pattern of MnCO_3 obtained from sulfuric acid system

The overall metal separation process is shown in Fig. 15. Since the waste material used in this study is a complex mixture of cobalt-nickel and zinc-manganese batteries, the Mn content is very high and the content of Co and Ni are relatively low. This situation leads to a difficult separation and recovery of Co and Ni, but an easy recovery of Mn. This study provides technical guidance for industrial recovery processes.

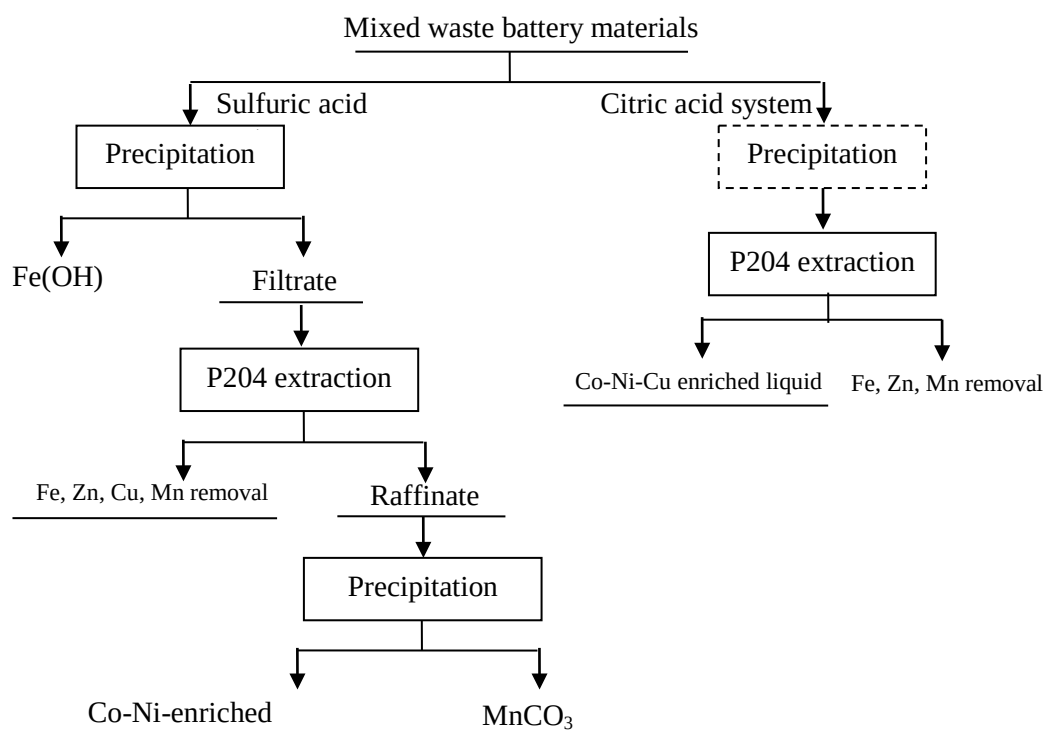


Fig. 15 Overall metal separation process

4. Conclusions

(1) Sulfuric and citric acids with hydrogen peroxide and potassium permanganate were used as medium to leach mixed waste battery material. Citric acid favors the dissolution of cobalt and nickel but is not conducive for the dissolution of the other metals. Potassium permanganate does not promote the dissolution of metals as an oxidant. The suitable leaching media is the citric acid-hydrogen peroxide system.

(2) According to the theoretical analysis, the metals do not precipitate in the citric acid system as easy as in the sulfuric acid system. Experimental studies have shown that the highest precipitation efficiency of Fe is 90% and occurred at pH 3.5. Since the content of Co and Ni are low in the raw

material, these metals precipitate 30% and 40% in the sulfuric acid system, respectively. In the citric acid system, the precipitation efficiency of Co, Ni, Mn, Fe, Cu and Zn are all less than 20% at pH 7, indicating that metal separation is difficult by precipitation.

(3) P204 was used in the sulfuric acid system and the citric acid system. The extraction order with increasing pH was Fe, Zn, Mn, Cu, Co and Ni in the sulfuric acid system. For Fe and Zn removal, the proper pH is 2 and the O/A ratio is 0.5, while for the removal of Cu and Mn the proper pH and O/A ratio is 3 and 0.75, respectively. The raffinate was selectively precipitated by ammonium carbonate solution to obtain crude MnCO_3 and Co-Ni-enriched liquid. At a pH of 1.5 and an O/A ratio of 2.0, the citric acid system favors metal separation in two groups; namely, Ni/Co/Cu and Mn/Fe/Zn, and a Co-Ni-Cu enriched liquid was finally obtained.

Acknowledgements

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