

Article

Experimental Study on Synergistic Extraction for Separating Manganese and Iron from Waste Ternary Battery Leaching Solution

Xuebin Peng ^{1,2,3}, Lei Shi ^{4,*} , Zhen Yang ^{2,3}, Lin Lin ^{2,3} and Tao Qu ¹
¹ Faculty of Metallurgy and Energy Engineering, Kunming University of Science and Technology, Kunming 650093, China

² State Key Laboratory of Advanced Metallurgy for Non-ferrous Metals, Kunming 650031, China

³ Kunming Metallurgical Research Institute Co., Ltd., Kunming 650031, China

⁴ Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China

* Correspondence: ahdyshilei@163.com

Abstract: In this paper, the key factors and the mechanism of the extraction of iron and manganese from the sulfuric acid leaching solution of waste ternary lithium-ion batteries were studied by combining P204 and N235 extractors. The experimental results showed that the optimal organic phase composition was 25% P204 + 15% N235 + 60% sulfonated kerosene, and the optimal pH of the pre-extraction solution was in the range of 3.0–3.5. Under the conditions of an extraction temperature of 25–35 °C and an extraction ratio of O/A = 1/1 and after mixing for 5 min, the removal rate of Mn and Fe exceeded 99%. Under the same extraction conditions, the extraction effect of the P204-N235 composite extractant on Mn and Fe was better than that of P204 alone. $\log D$ - $\log[P204]$ showed that the formulas of the Mn and Fe extracts were $MnR_2(HR)$ and $FeR_2(HR)$, respectively. The $\log D$ -pH diagram showed that only one free H^+ was released for each metal ion during extraction, and extraction occurred via a cation exchange reaction.

Keywords: P204; N235; collaborative extraction; removal rate



Citation: Peng, X.; Shi, L.; Yang, Z.; Lin, L.; Qu, T. Experimental Study on Synergistic Extraction for Separating Manganese and Iron from Waste Ternary Battery Leaching Solution. *Separations* **2023**, *10*, 265. <https://doi.org/10.3390/separations10040265>

Academic Editor: Guoquan Zhang

Received: 23 March 2023

Revised: 14 April 2023

Accepted: 17 April 2023

Published: 19 April 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The leaching solution of waste ternary batteries using the sulfuric acid system generally contains impurity elements such as Fe^{2+} and Mn^{2+} [1–10]. Fe^{2+} and Mn^{2+} should be removed before extracting valuable metals such as Ni and Co [7]. During wet smelting, Fe^{2+} and Mn^{2+} are mainly removed via oxidation and extraction separation [11–16]. The oxidation methods of Fe^{2+} include H_2O_2 oxidation [17–20], air oxidation [21], and $NaClO_3$ oxidation [22,23]. Because H_2O_2 easily decomposes, its oxidation rate is not high. The reaction time of air oxidation is long, and the oxidation effect is poor. $NaClO_3$ oxidation has a good oxidation effect, but $NaClO_3$ is prone to explosions due to friction and collisions with organic matter and reducing materials. There are two oxidation methods for removing Mn^{2+} : $KMnO_4$ oxidation [24,25] and H_2O_2 oxidation [26]. $KMnO_4$ oxidation is too strong, which makes the oxidation process difficult to control. When oxidizing Mn^{2+} , Ni^{2+} is also oxidized in large quantities, resulting in a high nickel loss rate. Oxidizing Mn^{2+} with H_2O_2 results in large consumption and high costs. Diluting the $NiSO_4$ solution reduces the Ni^{2+} concentration of the system, and the energy consumption of the subsequent system will be increased. Oxidation processes remove only some Fe^{2+} and Mn^{2+} . The obtained $NiSO_4$ solution cannot meet the content requirements of Fe^{2+} and Mn^{2+} for producing battery-grade $NiSO_4$ or electrolytic nickel, and the nickel loss rate is relatively high.

Solvent extraction methods can be carried out at a low temperature, and, using them, the solution can be deeply purified, and a high-purity $NiSO_4$ solution can be obtained.

In addition, the extraction agents can be recycled, and the cost is low. These methods can be easily scaled up to large-scale production. Commonly used extractants include acidic phosphine extractors, such as Cyanex272, P507, and P204, and alkaline amine extractors, such as N235 [27–32]. Acid phosphine extraction discharges large amounts of ammonia nitrogen wastewater during metal extraction. The amine extraction method is affected by the mechanism of metal ion extraction. Metal ions must form complex anions before they can be extracted, and the resulting raffinate has low solubility in the organic phase and easily forms a third phase, thus reducing the amount of extracted metal ions. Although traditional P204 saponification and N235 saponification extraction methods keep the acid in the aqueous phase, they produce a large amount of ammonia nitrogen wastewater. The saponification extraction method is adopted, instead of the combined extraction method, to avoid the saponification of acid phosphine extractants, thus producing no ammonia nitrogen wastewater. This maintains a high extraction rate and prevents environmental pollution.

The main purpose of this study was to use the properties of tertiary amine N235 extraction acid and acid phosphine extractant P204 to extract Fe and Mn. With 260# sulfonated kerosene as the diluent, a P204-N235 complex unsaponifiable extraction system was prepared to realize the green and low-energy extraction separation of Fe and Mn impurities from a NiSO_4 solution.

2. Experimental Section

2.1. Materials and Equipment

Crude NiSO_4 solution was obtained from waste NMC-811 (Nickel (N), Manganese (M), and cobalt (C) composite) lithium battery by pressurized reduction leaching during comprehensive recovery. The main phase composition of waste NMC-811 ternary lithium battery is shown in Figure 1. Figure 2 shows that the liquid was grass green. Tables 1 and 2 show the main phase composition and leaching and the liquefaction analysis results of waste NMC-811 ternary lithium batteries.

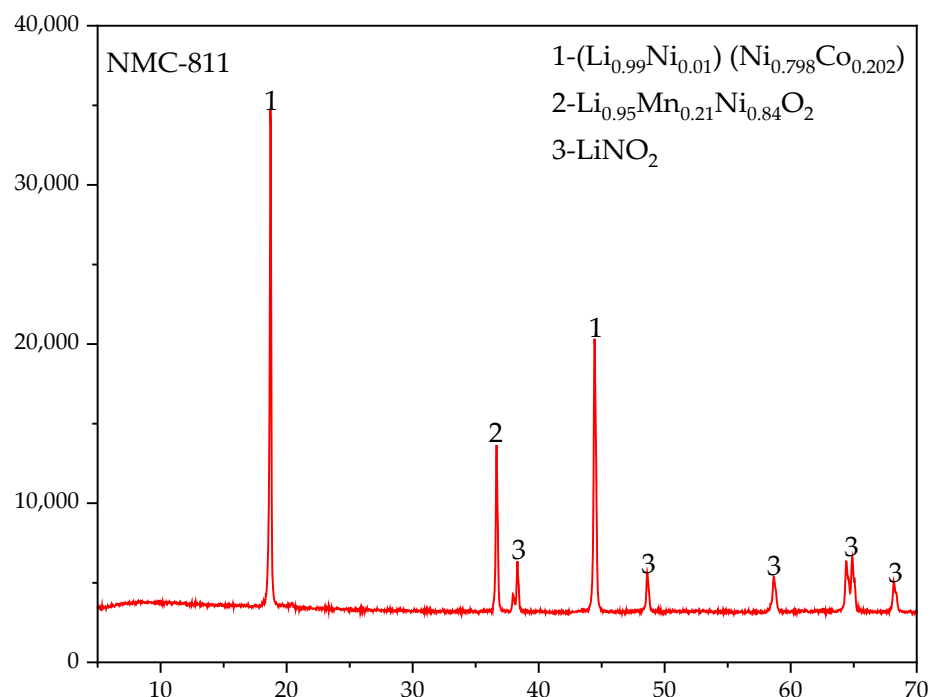


Figure 1. XRD pattern of the waste NMC-811 ternary lithium battery.



Figure 2. Pressurized leaching solutions.

Table 1. Main phases of waste NMC-8111 ternary lithium battery.

Phase	Content (%)
LiNO ₂	9.03
Li _{0.95} Mn _{0.21} Ni _{0.84} O ₂	43.19
(Li _{0.99} Ni _{0.01}) (Ni _{0.798} Co _{0.202})	46.78
Other	1.00

Table 2. Analysis results of waste NMC-811 leaching solution.

Material	Ni	Co	Mn	Fe	Li
NMC811 waste raw material (%)	49.56	5.69	5	0.52	6.67
Leaching solution (g/L)	45.81	4.16	0.19	0.26	2.36

During the extraction of Ni, Co, Li, and other valuable metals from waste lithium-ion batteries by pressurized acid leaching, the obtained leaching solution mainly contained Ni, Co, and Li, as well as the impurity elements Fe and Mn. No other impurity elements were detected.

The main instruments included a thermometer, a pH meter, a pear-shaped separator funnel, a beaker, and a AA-7000 Shimadzu atomic absorption spectrophotometer.

The chemical reagents included P204 produced by Luoyang Sanuo Chemical Co., Ltd. (Luoyang, China); N235 produced by Guangzhou Hongcheng Biotechnology Co., Ltd. (Guangzhou, China); industrial-grade NaOH produced by Junzheng Group (Wuhai, China); 98% H₂SO₄ produced by Yunnan Copper Industry (Kunming, China); and No. 260 sulfonated kerosene produced by Jinan Shengda Chemical Industry Co., Ltd (Jinan, China).

2.2. Test Principle

The molecular formula of extractant P204 (di-(2-ethyl hexyl) phosphoric acid) is (C₈H₁₇O)₂PO₂H, and its molecular structure is shown in Figure 3.

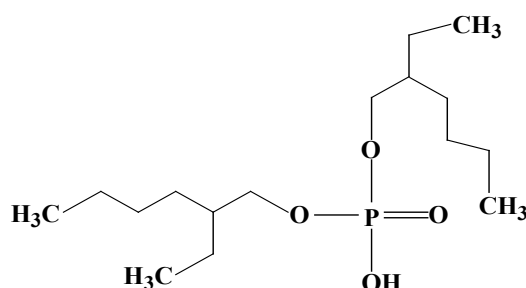
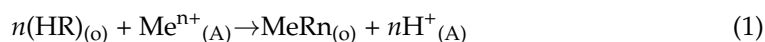


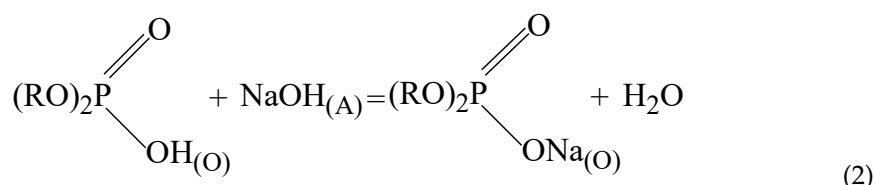
Figure 3. Molecular structure of P204.

Theoretical analysis of P204-N235 Extraction [33–35].

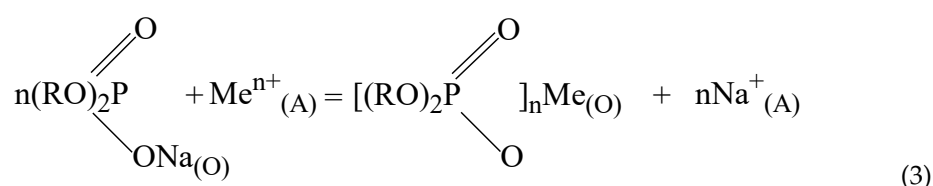
The mechanism of metal extraction includes a liquid cation exchange process:



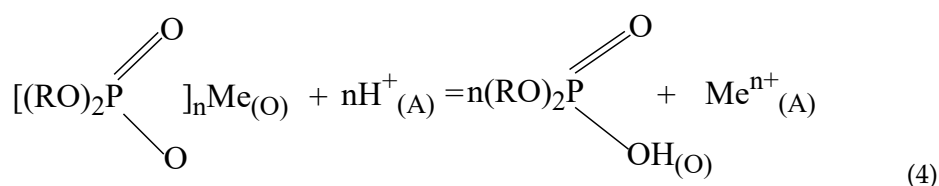
P204 Saponification:



P204 Extraction:

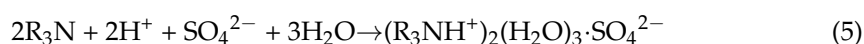


Back Extraction:



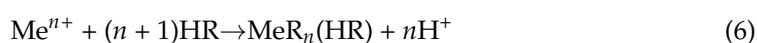
N235 extraction:

N235 is a tertiary amine extractant, which is alkaline and can extract H^{+} produced by P204 from the extraction of Fe and Mn elements. It can form some acid associations with N235 in sulfuric acid:



P204-N235 Collaborative Extraction:

According to the law of charge conservation, the anions OH^{-} and SO_4^{2-} in the aqueous phase do not participate in the reaction, while N235 can only react with metal complex anions, i.e., N235 does not participate in the metal ion extraction reaction and only controls the acidity of the extraction system. P204 usually exists as a dimer HR in liquid–liquid extraction systems. However, in the composite extraction system, due to the weak acid–base coupling between P204 and N235, P204 exists as the HR monomer, similarly to the complex reaction between a monic acid and metal ions. Thus, the reaction formula for the extraction of metal ions Me^{n+} is as follows:



According to the properties of P204 and N235, they were used to extract Fe and Mn elements, respectively, from the NiSO_4 solution without producing pollution. The extraction curves are shown in Figure 4 [36,37].

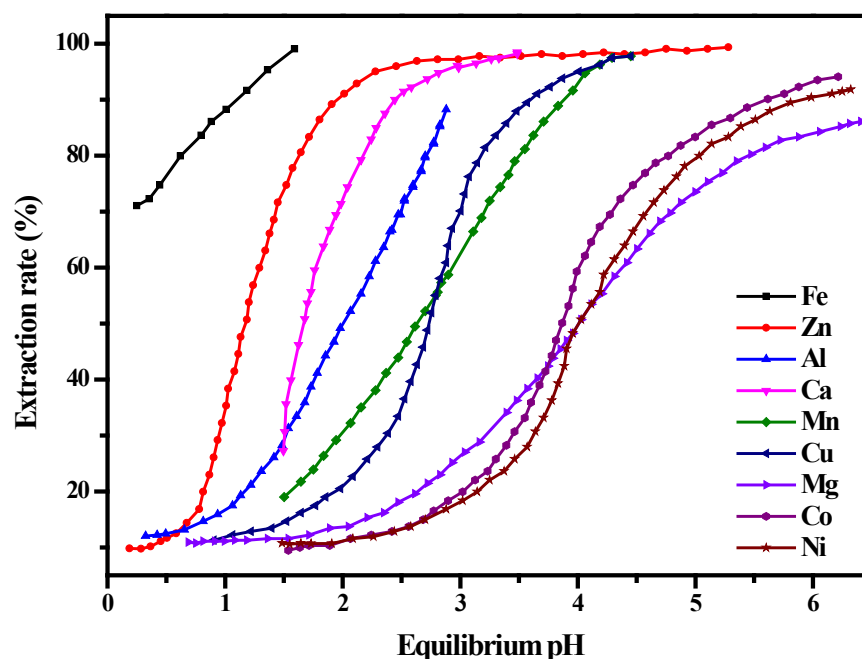


Figure 4. Extraction and separation curves of P204 at different pH values.

As shown in Figure 4, the order of various metals extracted by P204 from H_2SO_4 was $Fe > Zn > Ca > Al > Cu \approx Mn > Co > Mg > Ni$. Therefore, impurities such as Fe, Zn, Ca, Al, Cu, and Mn were extracted before Co and Ni, while Co and Ni remained in the raffinate. Li was not extracted and remained in the raffinate.

2.3. Process Flow Chart

The process flow chart is shown in Figure 5.

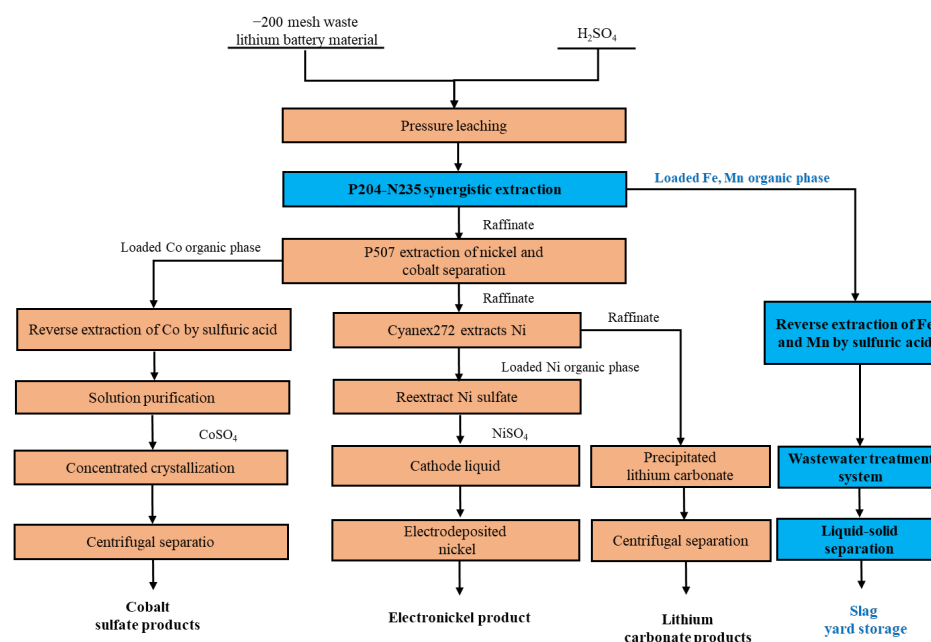


Figure 5. Process flow chart.

The leaching solution obtained by the pressurized acid leaching of waste lithium-ion batteries only contained Fe and Mn impurity elements. To remove Fe and Mn impurities from the leaching solution, the extraction separation method is generally adopted. After Fe

and Mn impurities were separated and removed by P204-N235 synergistic extraction, the contents of Fe and Mn in the raffinate were controlled to within 0.001 g/L. The solutions obtained by extracting Ni, Co, and Li from the purified solution by P507 and Cyanex272 can be used to produce NiSO_4 , CoSO_4 , Li_2CO_3 , respectively, in addition to electrolytic nickel products. P204-N235 organic phase loaded with Fe and Mn was reverse-extracted by sulfuric acid, and the organic phase was returned to the system for recycling. The reverse extract entered the wastewater treatment system for neutralization and precipitation separation. Fe- and Mn-containing slag were obtained and transported to the slag yard for storage, and the wastewater was discharged according to standards.

2.4. Experimental Methods

(1) Purification of P204 [38,39]

P204 and 1 M H_2SO_4 were mixed in a 1:1 volume ratio. After mixing for 5 min, the mixture was allowed to stand. After phase separation was complete, oil and water were separated. Equal volumes of 30% NaOH solution and P204 were mixed for 5 min and allowed to stand until phase separation was complete. Then, oil–water separation was performed three times. The solution was completely saponified, and, then, 6 M HCl was added, mixed, stirred, and acidified for 5 min. The solution was allowed to stand until phase separation was complete. Then, oil–water separation was performed, and P204 was washed with deionized water to neutrality. According to the calculated concentration, a certain volume of P204, N235 extractants, and diluent (sulfonated kerosene) were evenly mixed to prepare the required P204-N235 organic phase.

(2) Extraction

The P204-N235 organic phase was poured into the crude NiSO_4 solution for which pH was adjusted according to the O/A ratio. After mixing and extracting at a constant rotation speed, the mixed solution was transferred into a liquid separation funnel and allowed to stand until the organic phase and the aqueous phase were completely separated and a phase interface was clearly visible. The P204-N235 organic phase loaded with metal impurities and the raffinate were obtained by oil–aqueous phase separation. After reaching the extraction equilibrium, the supported organic phase in the liquid separation funnel was extracted twice with equal volumes of 1 M H_2SO_4 and 6 M HCl. When the organic phase and the aqueous phase formed a clear phase interface, the lower solution (reverse extract) was released. The organic phase after stripping was washed with deionized water four times until the pH of the aqueous phase was close to neutral to obtain the regenerated extractant. The effects of pH value, concentration of N235, concentration of P204, and extraction time on the extraction process of Fe and Mn were investigated; the organic phases before and after extraction were analyzed by infrared spectrum; and Ni, Co, Mn, and Fe were analyzed by sampling the raffinate. The extractive removal rate of Me^{n+} of each metal ion was calculated based on the concentration of Ni, Co, Mn, and Fe in the raffinate.

2.5. Analysis Method

The metal content was analyzed by filtering the analysis solution to remove trace suspended matter. Then, 5 mL solution was filtered and put into a 250 mL volumetric flask. The solution was injected into an AA-7000 Shimadzu atomic absorption spectrophotometer to detect the metal content.

2.6. Evaluation Indicators

The contents of Fe and Mn in the raffinate were analyzed by flame atomic absorption spectrometry, and the extraction removal rates of Fe and Mn were calculated as ω_{Me} .

Me extraction removal rate ω_{Me} :

$$\omega_{\text{Me}} = \left(\frac{A_0 - A}{A_0} \right) \times 100\% \quad (7)$$

where A_0 is the initial concentration of Me in the solution, g/L; A is the concentration of Me in the raffinate, g/L; ω_{Me} is the extraction removal rate of Me, %.

3. Experimental Results and Discussion

3.1. Influence of pH of the Pre-Extraction Solution on the Extraction Efficiency of Fe and Mn

The pH of the crude NiSO_4 solution (200 mL) was adjusted using H_2SO_4 . After pH was adjusted, the solution was the pre-raffinate. A two-stage countercurrent extraction was carried out using 25%P204 + 15%N235 + 60% sulfonated kerosene organic phase and an extraction temperature of 25–35 °C. The P204-N235 organic phase was poured into a NiSO_4 solution, and the pH was adjusted according to the extraction ratio of $\text{O}/\text{A} = 1/1$. At a constant rotation speed, a mixed extraction was carried out for 5 min at each stage. The mixed solution was transferred into a liquid separation funnel and allowed to stand until the organic phase and the aqueous phase were completely separated and a phase interface was clearly visible. Oil–water separation was then carried out, and the P204-N235 organic phase and the raffinate loaded with Me^{n+} were obtained. The P204-N235 organic phase loaded with Me^{n+} was recycled and used in the back extraction section. Fe, Mn, Co, and Ni contents were analyzed in the raffinate, and the influence of the pre-raffinate pH on the extraction rate of Me^{n+} was investigated. The experimental results are shown in Figure 6.

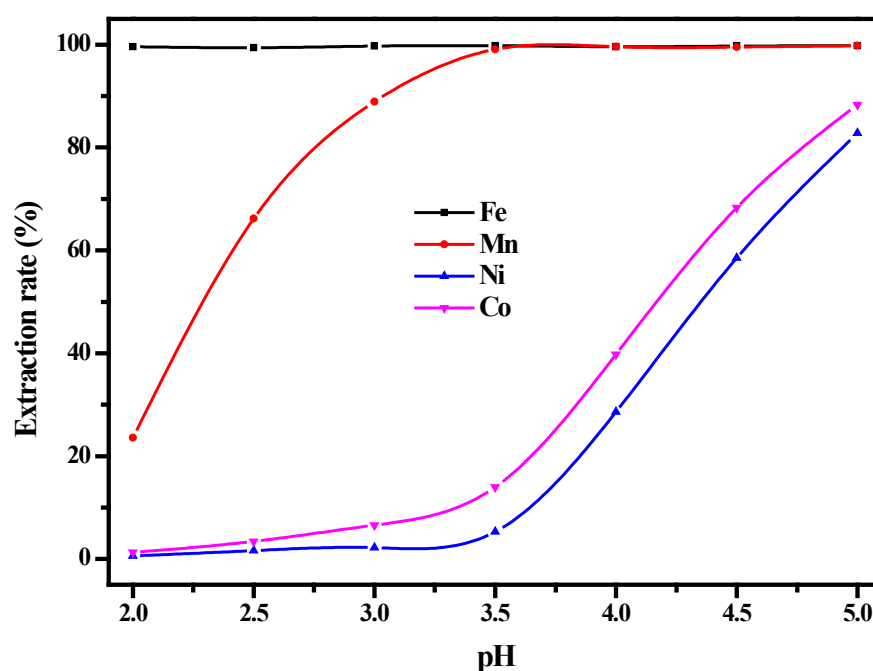


Figure 6. Effect of pH of the P204 extract on the removal rates of Fe and Mn.

As can be seen from Figure 6, the synergic extraction efficiency of metal ions such as Fe, Mn, Co, and Ni from the crude NiSO_4 solution by the P204-N235 composite extractor increased with the pH before extraction, i.e., the removal rate of Fe and Mn increased, while the direct yield of Co and Ni decreased. Therefore, performing extraction at a higher pH improved the synergistic extraction rate of Fe and Mn using the P204-N235 complex extractant. However, the extraction rate of Co and Ni also increased, which decreased the separation of Fe and Mn from Co and Ni. Near a pH of 3.5, the extraction rate of Fe and Mn exceeded 99.00%, the direct yield of Co was >85%, and the direct yield of Ni was >95%. The optimum pH of the raffinate was 3.5.

3.2. Influence of N235 Concentration on the Extraction Efficiency of Fe and Mn

The pH of 200 mL of the crude NiSO_4 solution was adjusted to 3.5 using H_2SO_4 . After pH was adjusted, the solution was the pre-raffinate. P204-N235-sulfonated kerosene

was taken as the complex organic phase. The volume fraction of P204 was 25%, and the volume fraction of N235 was controlled to within 5–35%. A two-stage countercurrent extraction was carried out, and the P204-N235-sulfonated kerosene complex organic phase was poured into a NiSO_4 solution (pH 3.5) according to the extraction ratio of $O/A = 1/1$. At a constant rotation speed, a mixed extraction was carried out for 5 min at each stage. The mixed solution was transferred into a separatory funnel and allowed to stand until the organic phase and the aqueous phase were completely separated and the phase interface was clearly visible. The P204-N235 organic phase and the raffinate loaded with metal ions Me^{n+} were obtained by oil–water separation. The P204-N235 organic phase loaded with Me^{n+} was recycled and used in the back extraction section. Fe, Mn, Co, and Ni contents were analyzed in the raffinate samples to investigate the effect of the N235 content in the P204-N235-sulfonated kerosene complex organic phase on the extraction rate of Me^{n+} . The experimental results are shown in Figure 7.

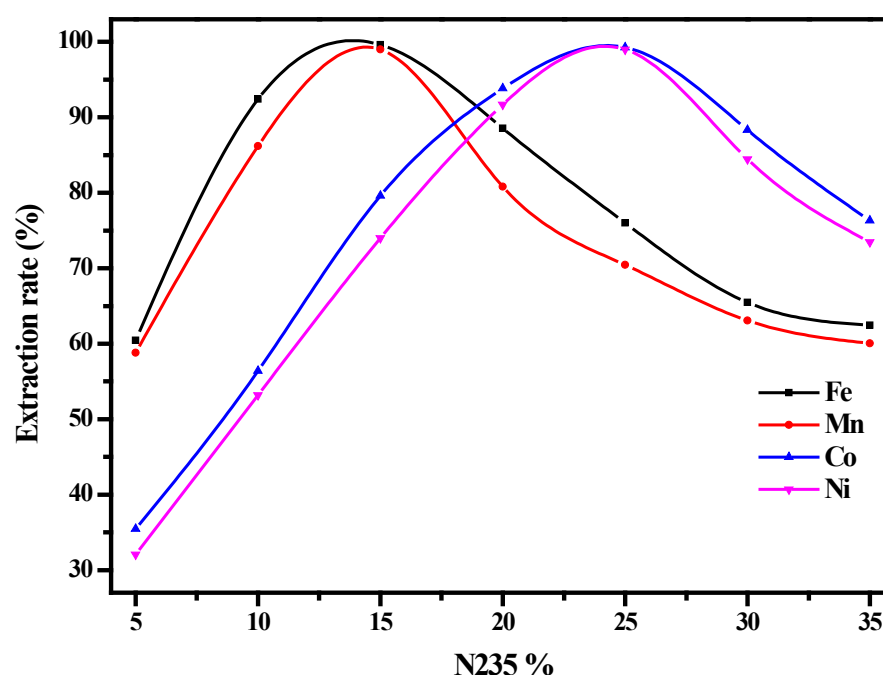


Figure 7. Effect of N235 concentration on the extraction of Fe and Mn by composite extractant.

As can be seen in Figure 7, upon increasing the N235 concentration, the extraction amount of P204-N235-sulfonated kerosene composite organic relative to Fe, Mn, Co, and Ni increased first and then decreased. This was because the viscosity of the composite organic phase increased gradually upon increasing the N235 content. A third phase was produced after a mixed extraction, which affected the extraction rate of Me^{n+} . This extended the static phase separation time. When the volume fraction of N235 was 15%, the saturated extraction amounts of Fe and Mn in the P204-N235-sulfonated kerosene complex were the highest, which were 50.2 mg (2.51 g/L) and 36.6 mg (1.831 g/L), respectively. When the concentration of N235 was in the range of 20–25%, the saturated extraction amounts of Ni and Co by the composite extractant were relatively high, which were 46.22 mg (2.311 g/L) and 60.26 mg (3.13 g/L), respectively. The loss rates of Ni and Co were too high, so the optimal volume fraction of N235 was 15%.

3.3. Effect of P204 Concentration on the Extraction Efficiency of Fe and Mn

The pH of 200 mL of the crude NiSO_4 solution was adjusted to 3.5 with H_2SO_4 . After pH was adjusted, the solution was the pre-raffinate. P204-N235-sulfonated kerosene was taken as the complex organic phase. The volume fraction of N235 was 15%, and the volume fraction of P204 was controlled within the range of 10–35%. A two-stage countercurrent

extraction was carried out, and the P204-N235-sulfonated kerosene complex organic phase was poured into a NiSO_4 solution with a pH of 3.5 according to the extraction ratio of $\text{O}/\text{A} = 1/1$. At a constant rotation speed, a mixed extraction was carried out for 5 min at each stage, and the mixed solution was transferred to a separatory funnel and allowed to stand until the organic phase and the aqueous phase were completely separated and a phase interface was clearly visible. The P204-N235 organic phase and the raffinate loaded with Me^{n+} were obtained by oil–water separation. The P204-N235 organic phase loaded with Me^{n+} was recycled and used in the back extraction section. Fe, Mn, Co, and Ni contents in the raffinate samples were analyzed to investigate the effect of P204 content in the P204-N235-sulfonated kerosene complex organic phase on the extraction rate of Me^{n+} . The experimental results are shown in Figure 8.

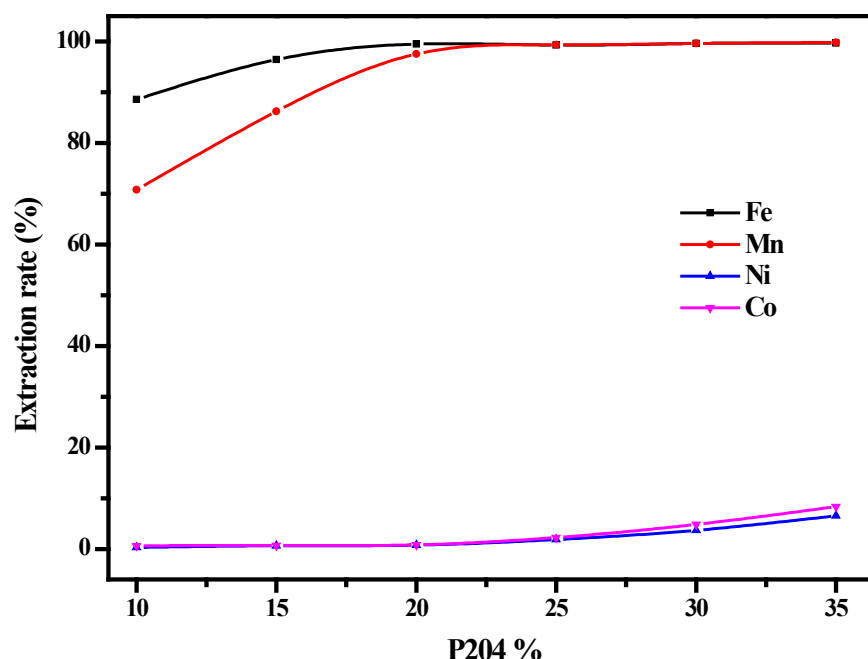


Figure 8. Effect of P204 concentration on the extraction efficiency of Fe and Mn.

Figure 8 shows that increasing the P204 concentration increased the extraction rates of Fe, Mn, Co, and Ni. When the volume concentration of P204 was 25%, the extraction rates of Fe and Mn increased gently, eventually exceeding 99%. In this case, the extraction rates of Ni and Co were 1.83% and 2.28%. Upon increasing the P204 concentration, the extraction rate of the P204-N235-sulfonated kerosene composite organics relative to the metal ions also increased. The loss of Co and Ni increased, the viscosity of the organic phase increased, and the static phase separation time was prolonged. A third phase was produced, which increased the organic phase loss. This may increase production costs and decrease the separation of metal impurities from Co and Ni. Therefore, the optimal P204 volume fraction in the organic phase was 25%.

3.4. Influence of Mixed Extraction Time on Extraction Efficiency of Fe and Mn

The pH of 200 mL of the crude NiSO_4 solution was adjusted to 3.5 with H_2SO_4 . After pH was adjusted, the solution was the pre-raffinate. P204-N235-sulfonated kerosene was taken as the complex organic phase (the volume fraction was 25% P204 + 15% N235 + 60% sulfonated kerosene). A two-stage countercurrent extraction was carried out, and the P204-N235-sulfonated kerosene complex organic phase was poured into a NiSO_4 solution at pH 3.5 according to the extraction ratio $\text{O}/\text{A} = 1/1$. At a constant rotation speed, the mixed phase was extracted for 1–7 min at each stage. The mixed solution was transferred into a separatory funnel and allowed to stand until the organic phase and the aqueous phase were

completely separated and a phase interface was clearly visible. The P204-N235 organic phase and the raffinate loaded with Me^{n+} were obtained by oil–water separation. The P204-N235 organic phase loaded with Me^{n+} was recycled and used in the back extraction section. The Fe, Mn, Co, and Ni contents in the raffinate were analyzed to investigate the effect of the mixed extraction time on the extraction rate of Me^{n+} . The experimental results are shown in Figure 9.

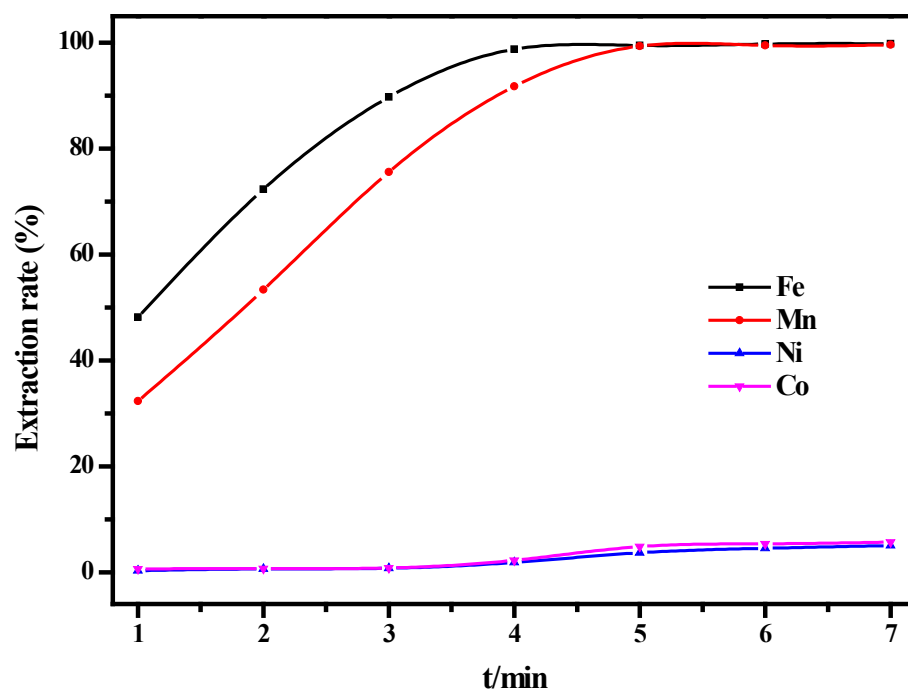


Figure 9. Effect of mixed extraction time on the extraction efficiency of Fe and Mn.

Figure 9 shows that, upon extending the mixed extraction time, the extraction rates of Fe and Mn increased rapidly at first and then stabilized. The extraction rates of Co and Ni increased gently within a narrow range. When the mixed extraction time was 5 min, the extraction rate curves of Fe, Mn, Ni, and Co all eventually stabilized at values of 99.46%, 99.36%, 3.68%, and 4.82%, respectively. Extending the mixed extraction time extended the time required for phase separation after extraction. After the mixing and extraction time exceeded 6 min, oil-in-water emulsification occurred and a third phase appeared. After standing for 5 min, the third phase disappeared, and the severely emulsified organic phase could be recycled only after regeneration. Upon extending the mixed extraction time, the two-phase reaction time was also lengthened, and the extraction rate of the metal ions by composite extractors increased accordingly. However, when the mixed extraction time was too long, emulsification occurred. Upon extending the phase separation time, the extraction amounts of Co and Ni gradually increased, and the loss rate also increased. Therefore, the optimal extraction time was 5 min.

3.5. Comparison of the Extraction Effect of P204 and Composite Extractant on Fe and Mn

The pH of 200 mL of the crude NiSO_4 solution was adjusted to 3.5 with H_2SO_4 . The solution with a good pH value was the pre-raffinate solution, which was mixed and extracted with a P204-N235-sulfonated kerosene complex organic phase (volume fraction 25% P204 + 15% N235 + 60% sulfonated kerosene) and P204-sulfonated kerosene organic phase (volume fraction 25% P204 + 75% sulfonated kerosene). Under the conditions of a controlled extraction with $\text{O}/\text{A} = 1/1$ and a countercurrent extraction, the P204-N235-sulfonated kerosene complex organic phase or the P204-sulfonated kerosene organic phase was poured into a NiSO_4 solution with a pH of 3.5 according to the extraction with $\text{O}/\text{A} = 1/1$. At a constant rotation speed, each stage was mixed and extracted for 5 min.

The mixed solution was transferred to a separatory funnel and allowed to stand until the organic phase and the aqueous phase were completely separated and a phase interface was clearly visible. Then, oil–water separation was carried out to obtain the organic phase and the raffinate loaded with Me^{n+} . The organic phase loaded with Me^{n+} was recycled and used in the back extraction section. Fe and Mn contents in the raffinate were analyzed, and the extraction effect of the P204-N235-sulfonated kerosene complex organic phase and the P204-sulfonated kerosene organic phase relative to Me^{n+} was investigated. The experimental results are shown in Table 3.

Table 3. Comparison of the effects of P204-N235 and P204 on Fe and Mn extraction.

Name	Extraction Rate %	
	Fe	Mn
P204-N235	99.86	99.82
P204	78.36	71.86

A comparative analysis of the data in Table 3 shows that the extraction effect of the P204-N235 compound extractant on Fe and Mn was significantly better than that of P204 alone.

3.6. Reproducibility Study

According to the optimal conditions determined by the above single-factor experiments, the organic phase composition volume of the synergic extractant P204-N235 was 25% P204 + 15% N235 + 60% sulfonated kerosene. For the two-stage countercurrent extraction, the pH of the pre-extraction solution was 3.0–3.5, the extraction temperature was 25–35 °C, the extraction ratio was O/A = 1/1, and the mixed extraction had a duration of 5 min. Three groups of reproducibility experiments were carried out, and the results are shown in Table 4.

Table 4. Reproducibility of P204-N235 synergistic extraction.

Experiment Number	Removal Rate/%		Raffinate (g/L)	
	Fe	Mn	Fe	Mn
Pre-extraction solution	/	/	0.26	0.19
1	99.92	99.84	0.0002	0.0003
2	99.96	99.89	0.0001	0.0002
3	99.88	99.79	0.0003	0.0004
Average	99.92	99.84	0.0002	0.0003

The analysis of the data in Table 4 shows that, under the optimized conditions, Fe and Mn were almost completely separated by the P204-N235 combined extraction, with removal rates of 99.92% and 99.84%, respectively. The average Fe content in the raffinate was only 0.0002 g/L, and the average Mn content was 0.0003 g/L.

3.7. Infrared Spectral Analysis of the P204-N235 Synergistic Extraction System

An infrared spectral analysis was performed for the P204-N235 synergistic extraction system on the organic phase before extraction and after collaborative extraction. The characterization results are shown in Figure 10, and the characteristic frequencies of selected peaks are shown in Table 5.

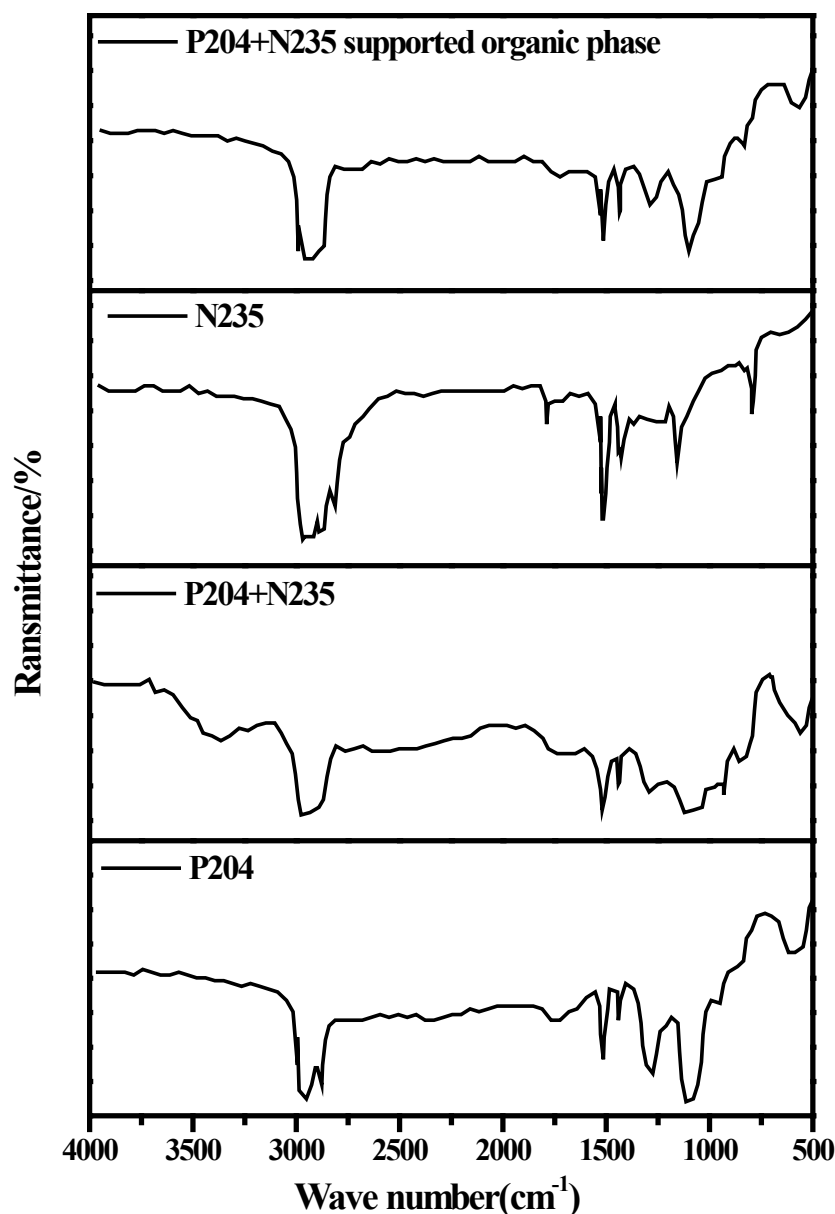


Figure 10. Infrared spectra of N235, P204, N235 + P204, and the loaded organic phase.

Table 5. Characteristic frequencies of infrared spectra of N235, P204, N235 + P204, and the extraction phase.

Characteristic Peak	Hydrogen Bonding in P204 Dimer	P=O	P=O=H
P204	1463	/	/
N235	/	1183	975
P204 + N235	/	1183	975
P204 + N235 loaded organic phase	1465	1175	959

Next, a comparative analysis of the infrared spectra was performed for the loaded organic phase, blank extractant N235, blank co-extractant P204-N235, and blank extractant P204 (Figure 10). The peak at 1183 cm^{-1} was caused by the P=O group, and the peak at 975 cm^{-1} was caused by the stretching and bending vibrations of the P-O-H bond.

By comparing the vibration absorption peak frequencies of the blank phase of P204-N235 and the loaded organic phase of P204-N235, the positions of the vibration absorption peaks in the infrared spectrum were varied. However, the changes in the absorption peaks indicate that H^+ in some P=O bonds was replaced by Me^{n+} , i.e., P-O groups were

formed. During the extraction of Me^{n+} , the P204 extractant mainly existed in the form of hydrogen-bonded dimers that covered its polar phosphate groups. These often participated in reactions in the form of dimers during complexation with metal ions.

The infrared spectra of blank P204, blank N235, and blank P204-N235 showed different absorption peak positions. The vibration frequency of P=O in the blank N235 spectrum was located at 1183 cm^{-1} , and the frequency decreased after adding P204. A red shift occurred after the extraction of metal ions such as Fe and Mn, i.e., the P=O bond moved to a lower wavenumber after extraction. This indicates that the P=O bond coordinated with Fe, Mn, and other metal ions. After P204 formed P-O-Re coordination bonds with Fe, Mn, and other metal ions, the electron cloud density of the P=O double bond decreased, and the bond strength weakened. This decreased its vibration frequency, which shifted the absorption peak of P=O to a lower wavenumber [40].

3.8. Mechanism Study on the Extraction of Fe and Mn by P204-N235 Combined Extractant

P204 has a low solubility in water, and the raffinate formed during the extraction has a high solubility in organic solvents but a low solubility in water. The mechanism of metal ion extraction by P204 is cation exchange. Hydrogen atoms of hydroxyl groups will exchange cations with the extracted metal. The resultant raffinate has a high solubility in the organic phase, i.e., it will be extracted into the organic phase. The phosphoacyl group-P=O in P204 has a lone pair of electrons and can coordinate with metal ions. When extracting metal ions, the reaction formula is:



where M represents metal ions, m represents the valence state of the metal ions, n represents the number of P204 needed to extract a metal ion, and HR represents the P204 extractant. The relationship between the equilibrium constant k_e and the partition ratio of the composite extractant for the extraction of Ni, Co, Fe, and Mn is as follows:

$$k_e = \frac{[HR_m(n - m)HR][H^+]^m}{[M^{m+}][HR]^n} \quad (9)$$

$$\log k_e = \log D + m \log[H^+] - n \log[HR] \quad (10)$$

$$\log D = \log k_e + mpH + n \log[HR] \quad (11)$$

The $\log D$ vs. $\log[P204]$ relationship between different P204 concentrations and the distribution ratios of Ni, Co, Fe, and Mn in the P204-N235 composite extraction system is shown in Figures 11 and 12. The equations used to fit the experimental curves are as follows:

$$\log D_{Ni} = -1.97 + 1.76 \log[P204] \quad R^2 = 0.9816 \quad (12)$$

$$\log D_{Co} = -1.87 + 1.75 \log[P204] \quad R^2 = 0.9673 \quad (13)$$

$$\log D_{Fe} = 0.093 + 1.2958 \log[P204] \quad R^2 = 0.9285 \quad (14)$$

$$\log D_{Mn} = 0.024 + 1.3421 \log[P204] \quad R^2 = 0.9264 \quad (15)$$

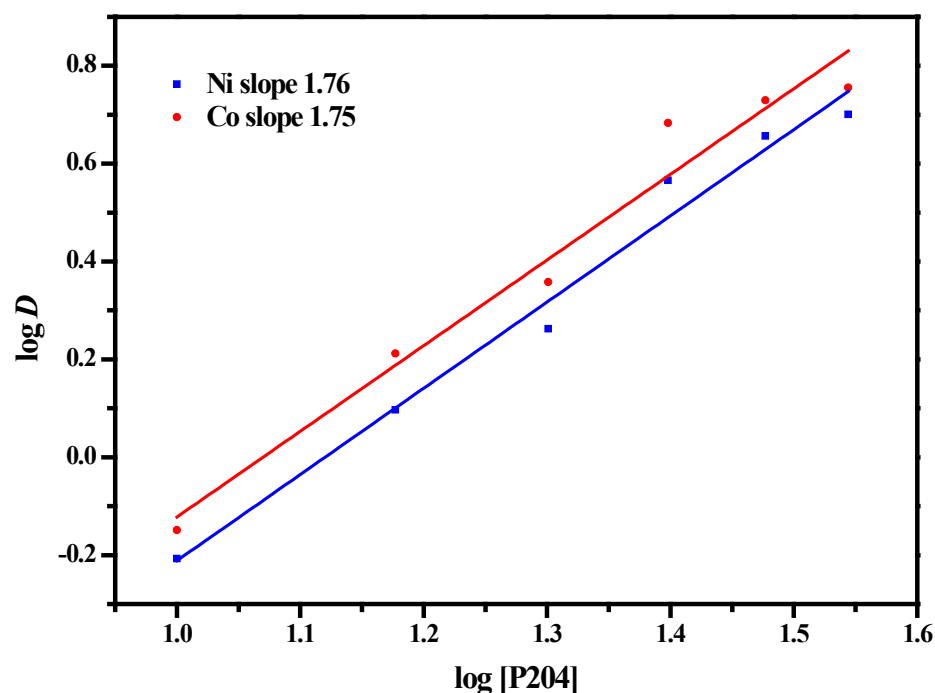


Figure 11. $\log D$ — $\log[P204]$ diagram of Ni and Co.

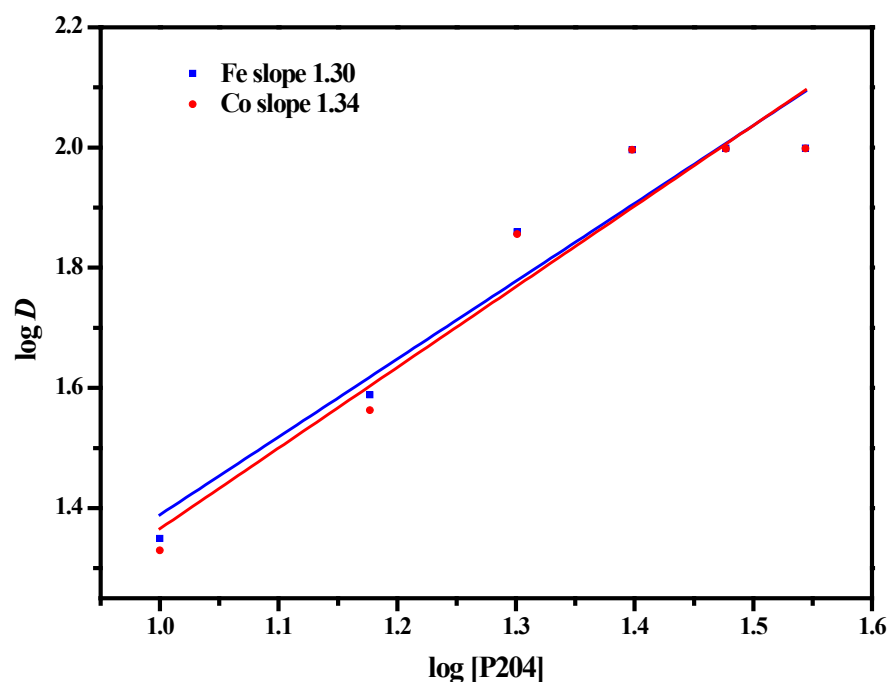


Figure 12. $\log D$ — $\log[P204]$ diagram of Fe and Mn.

The above equations show that the distribution ratio of Ni, Co, Fe, and Mn when using the composite extractant P204-N235 increased upon increasing the concentration of P204. The slopes of the equations of Ni, Co, Fe, and Mn were 1.76, 1.75, 1.30, and 1.34, respectively, indicating that two P204 molecules are required to extract each metal ion. Thus, $n = 2$ in Equation (8).

Increasing the concentration of P204 in the organic phase can increase the concentration and surface area of the reactants, accelerate the reaction rate, and increase the equilibrium conversion rate. When the equilibrium pH value was constant, $\lg D = 2\lg[HR] + C$, D is the metal allocation ratio. There is a linear relationship between $\lg D$ and $\lg[HR]$, and the

partitioning ratio increases with the extractant concentration, i.e., the extraction capacity also increased.

The $\log D$ vs. pH relationship between the distribution ratios of Ni, Co, Fe, and Mn extracted by the composite extractant P204-N235 and the pH of the aqueous phase is shown in Figure 13. The equations used to fit the experimental data are as follows:

$$\log D_{\text{Ni}} = -1.79 + 0.7641 \log[\text{P204}] \quad R^2 = 0.9705 \quad (16)$$

$$\log D_{\text{Co}} = -1.0789 + 0.6344 \log[\text{P204}] \quad R^2 = 0.9821 \quad (17)$$

$$\log D_{\text{Fe}} = 1.9028 + 0.02115 \log[\text{P204}] \quad R^2 = 0.9212 \quad (18)$$

$$\log D_{\text{Mn}} = 1.4675 + 0.1169 \log[\text{P204}] \quad R^2 = 0.9147 \quad (19)$$

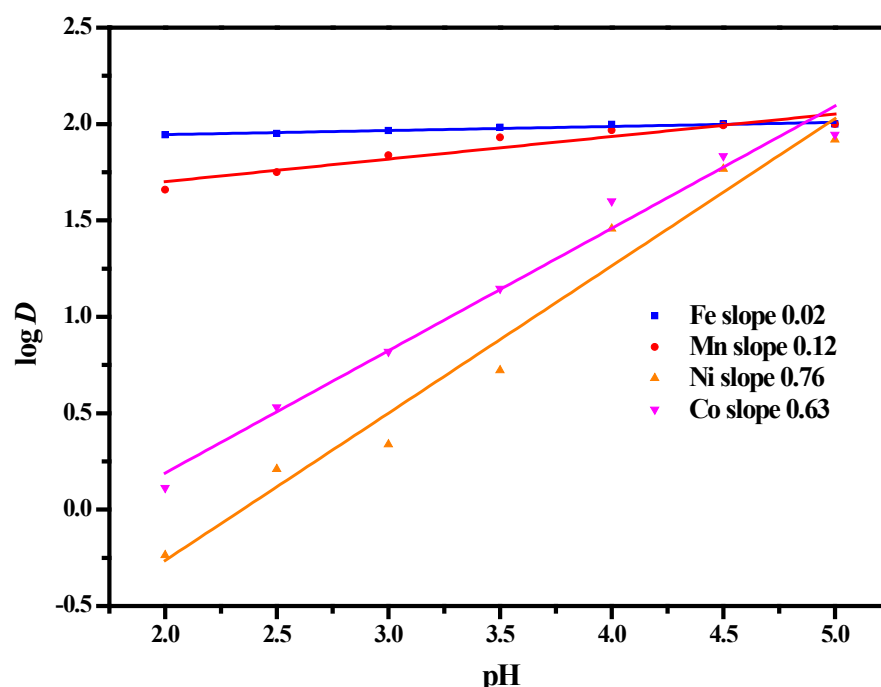


Figure 13. $\log D$ — $\log \text{pH}$ diagram of Fe and Mn.

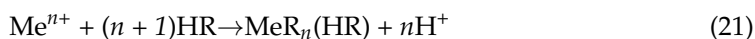
The above equations show that the distribution ratios of Ni, Co, Fe, and Mn in the composite extractant P204-N235 increased with the aqueous pH, and the slopes of Ni, Co, Fe, and Mn equations were 0.76, 0.63, 0.02, and 0.12, respectively. Because these are all within the range of 0–1, each metal ion extraction only released one free H^+ at most. Because N235 in the complex extractant is a tertiary amine extractant, it can extract H^+ generated when P204 extracts Ni, Co, Fe, and Mn. It can form an acid complex with N235 in sulfuric acid via the following equation:



P204-N235 Collaborative Extraction:

According to the law of charge conservation, OH^- and SO_4^{2-} in the solution do not participate in the reaction, while N235 can only react with metal complex anions, i.e., N235 does not participate in the extraction of metal ions and only regulates the acidity of the extraction system. P204 usually exists as a dimer HR in liquid–liquid extraction systems. However, in the complex extraction system, due to weak acid–base coupling between P204 and N235, P204 existed as the monomer HR, similarly to the complex reaction between

monic acid and metal ions. Therefore, every extracted metal ion, such as Fe and Mn, only released 1 free H^+ at most, and the other H^+ was extracted by N235 to form an acid complex. This also shows that the composite extraction mechanism of Fe, Mn, etc., involved a cation exchange reaction. Thus, the extraction reaction of Me^{n+} by the composite extractant P204-N235 is as follows:



According to the properties of P204 and N235, the two extractants were used for the extraction-separation of Fe and Mn from a $NiSO_4$ solution without polluting the environment.

4. Conclusions

- (1) When the organic phase composition volume of the synergic extractant P204-N235 is 25% P204 + 15%N235 + 60% sulfonated kerosene, a two-stage counter-current extraction of Mn and Fe can achieve a removal rate of more than 99%.
- (2) The optimal extraction condition of Fe and Mn with synergic extractant P204-N235 was 25% P204 concentration. Under the same extraction conditions, the compound extractant has a better extraction effect on Fe and Mn than P204 alone. It was concluded from the mechanism study that the composition of the Fe and Mn raffinates extracted by the composite extractants were $FeR_2(HR)$ and $MnR_2(HR)$, and the mechanism was a cation exchange reaction.
- (3) The P204-N235 collaborative extraction method is introduced to replace the P204 saponification extraction method in the waste battery recovery process, avoiding the saponification of acid phosphine extractants, so there will be no environmental pollution caused by the saponification of ammonia nitrogen wastewater. It not only maintains a high extraction rate but also has no harm to the environment, which is in line with the environmental protection concept of green, efficient, and sustainable development. This technology can provide technical support for the optimization of the waste battery recycling process. After optimization, it can reduce the saponification process, shorten the process flow, save energy, reduce consumption, and improve production efficiency. Overall, it has a high prospect for industrial application.

Author Contributions: Conceptualization, X.P., L.S. and L.L.; data curation, X.P.; formal analysis, X.P.; funding acquisition, L.S. and T.Q.; investigation, X.P. and L.L.; methodology, X.P. and T.Q.; resources, X.P.; software, X.P.; supervision, Z.Y.; validation, X.P. and Z.Y.; visualization, X.P.; writing—original draft preparation, X.P.; writing—review and editing, L.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work has been funded by the Academician Free Exploration Fund of Yunnan Fundamental Research Projects (No. 202201AU070194), Yunnan Province, China (No. 2022HA006) and the National Science Foundation of China (No. 52204362 and 52260020).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ouyang, S.B.; Li, Q.; Chen, R.K.; Chen, S.; Ruan, D.S.; Fang, B.L. Using high temperature roasting—Sulfuric acid leaching process extract cobalt from waste battery materials. *J. Hydrometall.* **2020**, *33*, 304–308. [[CrossRef](#)]
2. Shi, L.H.; Sun, S.Y.; Lu, C.X.; Yang, F.; Li, H.M. Leaching of nickel cobalt manganese Lithium from waste ternary lithium ion battery materials with sodium sulfite. *Hydrometallurgy* **2018**, *5*, 384–387. [[CrossRef](#)]
3. Chen, H.; Zhang, Y.L.; Tan, Q.Y.; Tang, H.H.; Li, Q.; Liu, Q. Experimental study on High Pressure acid leaching of cobalt, nickel, manganese and Lithium from waste battery cathode material slag. *Hydrometallurgy* **2018**, *37*, 388–392. [[CrossRef](#)]

4. Zhu, X.F.; Zhao, R.R.; Chang, Y.; Chen, H.Y. Research on Acid Leaching of ternary Cathode Materials for waste lithium ion Batteries. *Batteries* **2017**, *47*, 105–108. [\[CrossRef\]](#)
5. Chen, S.B.; Cheng, L.X.; Zou, Y.F.; Kang, L.W. Using sulfuric acid leaching of cobalt from waste lithium battery test study. *J. Hydrometall.* **2015**, *34*, 32–34. [\[CrossRef\]](#)
6. Qiao, X.L.; Tian, J.; Ma, S.Y.; Zhao, D.J. Recovery of cobalt from waste lithium ion Batteries by acid leaching. *J. Harbin Univ. Sci. Technol.* **2011**, *16*, 106–109. [\[CrossRef\]](#)
7. Ismael, M.R.C.; Carvalho, J.M.R. Iron recovery from sulphate leach liquors in zinc hydrometallurgy. *Miner. Eng.* **2003**, *16*, 31–39. [\[CrossRef\]](#)
8. Zhou, J.; Qiu, L.; Li, Y.; Deng, Y.; Zhao, Q.; Hu, Y.; Guo, F.; Zhu, C.; Zhong, B.; Song, Y.; et al. High Value-Added Utilization of Waste Hydrodesulfurization Catalysts: Low-Cost Synthesis of Cathode Materials for Lithium-Ion Batteries. *Separations* **2022**, *9*, 449. [\[CrossRef\]](#)
9. Peng, X.; Shi, L.; Qu, T.; Yang, Z.; Lin, L.; Xie, G.; Xu, B. Kinetics of Ni and Co Recovery via Oxygen-Enriched Pressure Leaching from Waste Lithium-Ion Batteries. *Separations* **2023**, *10*, 64. [\[CrossRef\]](#)
10. Tawonezvi, T.; Nomnqa, M.; Petrik, L.; Bladergroen, B.J. Recovery and Recycling of Valuable Metals from Spent Lithium-Ion Batteries: A Comprehensive Review and Analysis. *Energies* **2023**, *16*, 1365. [\[CrossRef\]](#)
11. Whittington, B.I.; Muir, D. Pressure Acid Leaching of Nickel Laterites: A Review. *Miner. Process. Extr. M.* **2000**, *21*, 527–599. [\[CrossRef\]](#)
12. Xu, G.X.; Yuan, C.Y. *Rare Earth Extractant Solvent Extraction of Rare Earth*; Sciences Press: Beijing, China, 1987; pp. 303–304, ISBN 9787030273451.
13. Wang, C.Y.; Wang, H.Y.; Jiang, P.H.; Yin, F.; Chen, Y.Q. P204 extraction separation of cobalt ferromanganese experimental study. *J. Non-Ferr. Met. Smelt.* 2006, pp. 2–5. Available online: <https://kns.cnki.net/kcms/detail/detail.aspx?FileName=METE200605001&DbName=CJFQ2006> (accessed on 6 June 2022).
14. Kongolo, K.; Mwema, M.D.; Banza, A.N. Cobalt and zinc recovery from copper sulphate solution by solvent extraction. *Miner. Eng.* **2003**, *16*, 1371–1374. [\[CrossRef\]](#)
15. Luo, L.; We, J.H.; Wu, G.Y. Extraction studies of cobalt (II) and nickel (II) from chloride solution using PC88A. *Trans. Nonferr. Metal. Soc.* **2006**, *16*, 687–692. [\[CrossRef\]](#)
16. Filiz, M.; Sayar, N.A.; Sayar, A.A. Extraction of cobalt(II) from aqueous hydrochloric acid solutions into alamine 336–m-xylene mixtures. *Hydrometallurgy* **2005**, *81*, 167–173. [\[CrossRef\]](#)
17. Li, J.H.; Li, X.H.; Zhou, Y.Y.; Hu, Q.Y.; Zhang, M.; Zhang, L.X. Purification of Leaching Solution of Spent NixCoyMnz Battery Material by Removing Cu and Fe. *Chin. J. Process Eng.* **2009**, *9*, 676–682.
18. Sun, Y.L.; Li, T.; Huang, X.; Tang, K.; Yu, Z.X.; Jin, Y.Z. Study on removal of iron from Cobalt Solution. *Chem. Eng. N. Y.* **2008**, *11*, 4–6. [\[CrossRef\]](#)
19. Zhang, W.S.; Shi, C.J.; Mei, G.G. Several main methods of iron removal in hydrometallurgy (including Zn, Mn, Cu, Ni, Co, etc.). *Manganese Ind. China* **2006**, *02*, 40–42.
20. Zhang, A.L.; Yang, C.F.; Fu, Y.; Zhai, X.J. Copper factory is a by-product of iron nickel sulfate study. *J. Nonferrous Min. Metall.* **2001**, *02*, 23–26.
21. Xu, X.L.; Tang, G.Z.; Yang, X.S. Containing bismuth chloride solution of air oxidation of iron research. *J. Jiangxi Nonferrous Met.* **1994**, *01*, 35–38.
22. Chen, C.H. Study on the process of removing Ferrous Metal by Electrolytic Manganese. *China Manganese Ind.* **1992**, *10*, 40–42.
23. Chen, H.; Zhang, Y.L.; Tan, Q.Y.; Tang, H.H.; Li, Q. Study on removal of iron and aluminum from Nickel-cobalt-manganese sulfate solution in waste battery recovery process. *Hydrometallurgy* **2018**, *37*, 482–486. [\[CrossRef\]](#)
24. Liu, B.; Tao, Y.; Zhou, Q. Application of potassium permanganate preoxidation technology to water treatment. *Shanxi Archit.* **2010**, *36*, 191–192.
25. Tang, M.; Ding, L.; Wu, J.F. Optimization of manganese removal by potassium permanganate in production and application. *Urban Water Supply* **2007**, *01*, 35–36.
26. Zhang, J.; Dai, Z.S. Principle and application of strong Oxidizer for manganese removal. *Water Supply Drain.* **1997**, *03*, 16–18.
27. Kumbasar, R.A. Selective extraction and concentration of cobalt from acidic leach solution containing cobalt and nickel through emulsion liquid membrane using PC-88A as extractant. *Sep. Purif. Technol.* **2009**, *64*, 273–279. [\[CrossRef\]](#)
28. Koladkar, D.V.; Dhadke, P.M. Cobalt-Nickel Separation: The Extraction of Cobalt(II) and Nickel(II) with Bis(2-Ethylhexyl) Phosphinic acid (PIA-8) in Toluene. *Solvent. Extr. Ion. Exc.* **2001**, *19*, 1059–1071. [\[CrossRef\]](#)
29. Reddy, B.R.; Priya, D.N. Chloride leaching and solvent extraction of cadmium, cobalt and nickel from spent nickel-cadmium, batteries using Cyanex 923 and 272. *J. Power Sources* **2006**, *16*, 1428–1434. [\[CrossRef\]](#)
30. Nayl, A.A. Extraction and separation of Co (II) and Ni (II) from acidic sulfate solutions using Aliquat 336. *J. Hazard. Mater.* **2010**, *173*, 223–230. [\[CrossRef\]](#)
31. Majdan, M.; Mierzwa, J.; Sadowski, P. On the separation of Co and Ni from chloride media with Aliquat 336-TBP and Aliquat 336-TOPO. *Mon. Für Chem. Chem. Mon.* **1997**, *128*, 113–121. [\[CrossRef\]](#)
32. Darvishi, D.; Haghsheenas, D.F.; Alamdari, E.K.; Sadrnezhad, S.K.; Halali, M. Synergistic effect of Cyanex 272 and Cyanex 302 on separation of cobalt and nickel by D2EHPA. *Hydrometallurgy* **2005**, *77*, 227–238. [\[CrossRef\]](#)
33. Zhang, Y.Z.; Cai, C.Q. Comprehensive recovery of cobalt-containing hard alloy waste. *Min. Metall. Eng.* **2000**, *20*, 34–36.

34. Niu, C.W.; Wang, K.Y.; Shu, W.L. In non equilibrium solvent extraction separation of cobalt and nickel study. *J. Non-Ferr. Met. Smelt.* **2000**, *4*, 6–8.
35. Qiu, Y.X. Study on the Separation of Copper, Nickel, Cobalt, Zinc and Cadmium from Wastewater by Versatic10/Mextra1984H. Master's Thesis, Beijing General Research Institute of Nonferrous Metals, Beijing China, 2014.
36. Xu, Z.G.; Wang, L.J.; Wu, M.; Xu, Y.L.; Chi, R.; Li, P.H.; Zhao, J. Separation of zirconium and hafnium by solvent extraction using mixture of DIBK and P204. *Hydrometallurgy* **2016**, *165*, 275–281. [[CrossRef](#)]
37. Wang, X.; Chen, S.L. Research and Application of extractant in Nickel-Cobalt hydrometallurgy. *Nonferrous Met. World* **2021**, *22*, 23–25. [[CrossRef](#)]
38. Wan, J.X. Phosphate Organic Extractant and Solid-Liquid Extraction of Copper and Cobalt Nickel Research. Master's Thesis, Northwest Normal University, Lanzhou, China, 2009.
39. Chang, H.T. Basic Study on Extraction and Separation of Light Rare Earth Elements by P204-Hel-H3AOH System. Ph.D. Thesis, Northwest Normal University, Lanzhou, China, 2008.
40. Wu, S.T. Study on the Extraction of Neodymium and Gadolinium by P204- Additive Modified Extraction System. Master's Thesis, Nanchang Hangkong University, Nanchang, Jiangxi, China, 2018.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.