

Separation of valuable metals from mixed cathode materials of spent lithium-ion batteries by single-stage extraction

Yongjie Li, Qiang Fu, Hongyun Qin, Kun Yang, Junnan Lv, Qicheng Zhang,
Hui Zhang, Feng Liu, Xia Chen[†], and Ming Wang[†]

School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo 255049, China
(Received 26 January 2021 • Revised 26 April 2021 • Accepted 3 May 2021)

Abstract—With the intensity of resource scarcities and environmental problems, the disposal and recovery of spent lithium-ion batteries, especially recovery of valuable metals, becomes vital. In this work, a method of co-extracting nickel, cobalt, manganese and being separated from lithium by single-stage solvent extraction is proposed. The extraction and separation process of D2EHPA was studied. The effects of extractant concentration, saponification percentage, extraction time and O:A on the extraction efficiency of D2EHPA were systematically studied. Nearly 100% manganese, 94% cobalt and about 90% nickel were co-extracted and separated from lithium using D2EHPA in kerosene by single-stage extraction. The maximum value of separation factors ($\beta_{Ni/Li}$, $\beta_{Co/Li}$ and $\beta_{Mn/Li}$) was 13.03, 23.42 and 1904.24. The mathematical model of extraction of four ions was developed by combination of Levenberg-Marquardt method and Universal Global Optimization method. The proposed extraction model accurately fits the experimental data and helps to predict the extraction efficiency of each metal under the corresponding conditions.

Keywords: Mixed Cathode Materials, Spent Lithium-ion Batteries, Co-extraction, Extraction Model

INTRODUCTION

Lithium-ion batteries (LIBs) are widely used in mobile electronic products, new energy vehicles, energy storage, military and other fields; they have the advantages of high capacity, small size, fast charging speed and high security [1,2]. A large number of spent lithium-ion batteries are produced, which will result in serious environmental pollution and huge waste of resources if not properly disposed. Therefore, the recovery from mixed spent LIBs, especially recycling valuable metals from mixed spent ternary cathode materials, is of great significance and economic value [3].

The recycling methods of spent lithium-ion batteries are mainly pyrometallurgy and hydrometallurgy [4]. Although the process of pyrometallurgy is simple, it requires expensive equipment and is prone to air pollution. Compared with pyrometallurgy, hydrometallurgy has the characteristics of less waste discharge, high recovery efficiency, excellent metal selectivity, and high added value of products [5-8]. It is generally believed that this is a more sustainable research method with great potential [9-11]. As an important process of hydrometallurgy, solvent extraction with the advantages of easy operation, simple equipment [12-14] and high purity of metal ions obtained is widely used in recycling valuable metals from the leaching solution of mixed cathode materials of spent LIBs [15-17]. However, solvent extraction for recovering lithium ion from cathode materials of spent LIBs has been less investigated. The traditional recovery processes focus on the extraction of manganese, cobalt and nickel, but this often tends to the loss of lithium. There-

fore, our work explored a process of simultaneously extracting nickel, cobalt, manganese ions and thus separating them from lithium ions. Lithium ions in the raffinate phase were recovered, while the nickel, cobalt and manganese ions in the extraction phase were directly used in the regeneration of ternary cathode materials. Generally, existing extraction processes are challenged by problems in the co-extraction of manganese, cobalt and nickel and their separation from lithium. Few extractants can extract and separate multiple metal ions in a single-stage extraction [18]. The extractants used to extract transition metals cobalt or/and nickel are generally phosphonic acid, phosphonate ester and other acid extractants. Coll et al. [19] proposed a method for extracting and separating cobalt and nickel from chloride solutions. The ionic liquid extractant HJMT⁺-Cyanex272⁻ was used to separate nickel with cobalt by continuous counter-current extraction. The extraction efficiency of cobalt was greater than 99%, and that of nickel was 11%. Torkaman, et al. [20] compared a variety of extractants and found that extractant bis(2,4,4-trimethylpentyl)-phosphinodithioic acid (Cyanex301) led to an increase in extraction efficiency of cobalt from aqueous solution in the low concentration range from the diluted chloride solution. The extraction of cobalt or/and nickel can use not only acidic extractants but also alkaline extractants. Using triethylamine (TEA) [21] with an extractant concentration of 5% pH=4.5, the extraction efficiency of nickel can reach 99.6%. In contrast, trioctylamine (TOA) extractant is an appropriate extractant for cobalt extraction in chloride acidic aqueous solution [20]. However, whether the acidic or basic extraction agents, the extraction performance is excellent only for single metal. Therefore, it is necessary to select an extraction agent with good extraction performance for both nickel and cobalt ions. Acidic phosphonate ester extractant D2EHPA represents more interesting extraction sequence in that the extraction efficiency-pH curves

[†]To whom correspondence should be addressed.

E-mail: hgxychx@sdu.edu.cn, wangming@zhongxunhb.com

Copyright by The Korean Institute of Chemical Engineers.

of cobalt and nickel ion at acidic conditions ($\text{pH} < 6$) were very close [22], which means that under certain conditions both metal ions can be co-extracted efficiently. Extraction of manganese ions can also be generally achieved through phosphonate esters, for example, Joo et al. proposed a process for extracting and separating manganese from spent lithium battery leachate. Manganese ions are almost completely extracted using 25 vol% Versatic10 acid/20 vol% 2-ethylhexyl hydrogen (2-ethylhexyl)phosphonate (PC-88A) at $\text{pH} = 4.5$ [23].

The present manuscript describes a study of co-extracting nickel, cobalt and manganese from spent lithium-ion batteries and their separation from lithium. By adjusting the factors that affect extraction, lithium is separated from nickel, cobalt and manganese ions in a single-stage extraction. Through the extraction efficiency obtained under different extraction conditions, the combination of Levenberg-Marquardt method and Universal Global Optimization method is used for calculation to obtain the most suitable mathematical model. The mathematical model for extraction of nickel, cobalt, manganese and lithium ions has been established, which can help to directly obtain corresponding extraction results under different extraction conditions in the range studied. The proposed extraction model can fit the extraction data of metal ions well and faithfully predict the simultaneous extraction of nickel, cobalt, manganese, and lithium ions mixed in the aqueous phase.

EXPERIMENTAL

1. Materials and Reagents

Extractants of bis(2-ethylhexyl) hydrogen phosphate (D2EHPA,

Table 1. Elemental composition of the leaching solution

Metal ions	Ni^{2+}	Co^{2+}	Mn^{2+}	Li^+
Composition/($\text{g} \cdot \text{L}^{-1}$)	6.570	2.775	6.010	2.475

P204) (purity, 95%), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHEHPA, P507) (purity, 99%) and neodecanoic acid (purity, 98%) were all purchased from Shanghai Meryer Chemical Technology Co., Ltd. Sulfonated kerosene of industrial grade was used as diluent. Sodium hydroxide (NaOH) was used for saponification reaction. The simulated leachate of ternary cathode materials of mixed spent LIBs was synthesized by dissolving certain amount of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ with analytical grade in distilled water. The metal ion concentration in the prepared leaching solution as listed in Table 1 was obtained by our previous work [24] without any impurities.

2. Solvent Extraction

A method is proposed in Fig. 1 that recovers metals (Ni, Co, and Mn) one by one, while leaving Li in the raffinate. Considering 10 mL synthetic leachate to be extracted separation, D2EHPA was first mixed with sulfonated kerosene to obtain 40% volume concentration of extractant. The prepared organic phase was saponified by NaOH (saponification percentage 65%), oscillated at a constant speed on the oscillator for a while and a new organic phase was then obtained by a separation funnel. According to the ratio of organic phase to aqueous phase ($\text{O:A} = 1$), the saponified organic phase was mixed and reacted with 10 mL synthetic leachate under the uniform oscillation for 5 min. After a standing and stratifying process, the loaded organic phase and the raffinate were separated.

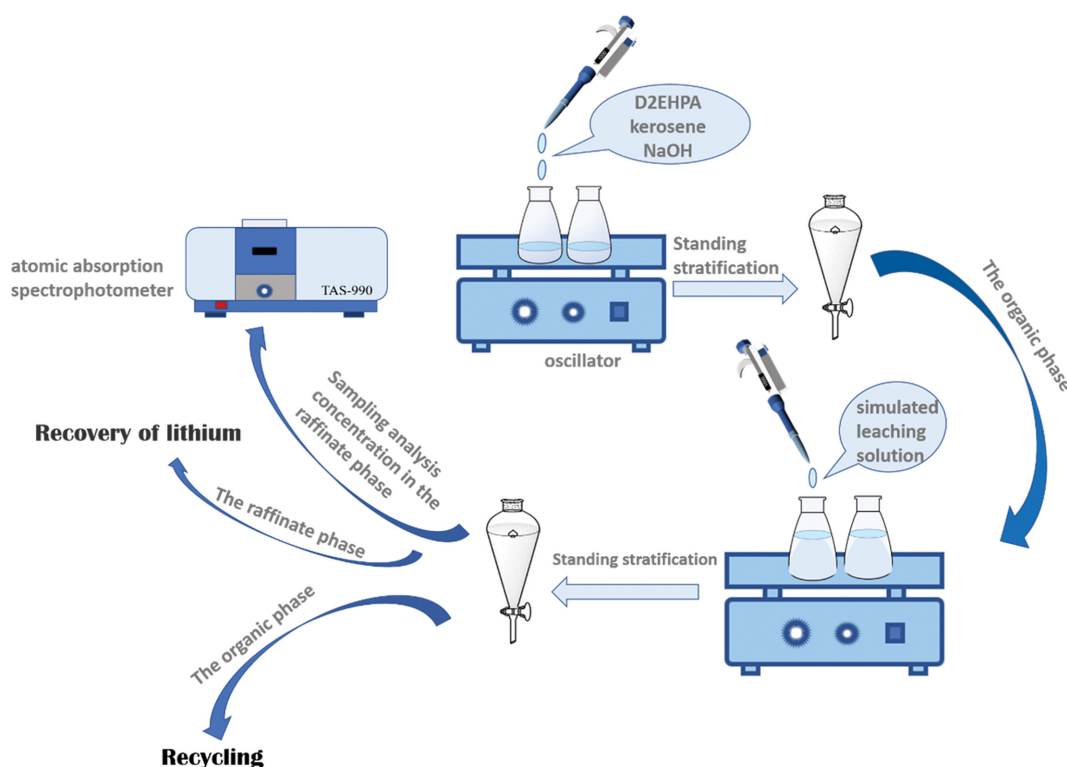
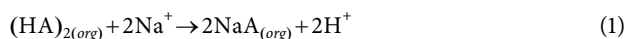


Fig. 1. Co-extraction of nickel, cobalt and manganese and separated with Lithium from mixed spent LIBs by single-stage extraction.

An atomic absorption spectrophotometer (TAS-990) was used to determine the concentration of metal ions in the raffinate. Before the measurement, a small quantity of the raffinate was diluted to a specific concentration with a volumetric flask. The dilution ratio is generally 1,000 times or more, which is subject to the experimental data.

The saponification percentage can be obtained according to the following Eq. (1) [25]:



Analyzing the concentration of metal ions in the raffinate and calculating the extraction efficiency of each metal ions according to formula (2):

$$E = \frac{C_0 V_0 - C_w V_w}{C_0 V_0} \times 100\% \quad (2)$$

where E stands for extraction efficiency; C_0 and C_w for metal concentration in the aqueous before/after extraction; V_0 and V_w for aqueous phase volume before/after extraction.

When the extraction reaction reached equilibrium, the distribution ratio and the separation factor were expressed as formula (3) and (4), respectively:

$$D = \frac{C_{org}}{C_w} \quad (3)$$

$$\beta = \frac{D_{Me,i}}{D_{Li}} \quad (4)$$

where D is distribution ratio; C_w and C_{org} stand for the concentration of certain metal ion in raffinate and loaded organic phase, respectively; β for the separation factor, $D_{Me,i}$ and D_{Li} for the distribution ratio of metal i and Li.

RESULTS AND DISCUSSION

1. Screening of Extractants

Acidic extractants are usually used in the extraction of transition metal ions such as nickel and cobalt ions [26]. The most widely used is D2EHPA, known as “universal extractant” [27] and EHEHPA, which is similar to D2EHPA in the ability of metal extraction but with better extraction selectivity [28]. Neodecanoic acid is often used to separate divalent and monovalent metal ions, and the extraction process is very fast [16]. The above three extractants were screened to co-extractive separation nickel, cobalt and manganese ions with lithium ions.

With extractants in sulfonated kerosene as organic phase, the performance of the three acidic extractants including extraction efficiency and separation factor was tested. Under the conditions of O:A=1, extractant volume concentration of 50%, saponification percentage of 65%, extraction oscillation time of 10 min, room temperature, the extraction effects of three extractants on four ions were compared. As shown in Fig. 2, under the same conditions, the three extractants all showed higher extraction efficiency for nickel, cobalt and manganese ions. The extraction efficiency of D2EHPA for the three ions was above 95%. The extraction efficiency of EHEHPA for the three ions was similar to that of D2EHPA, but they were all

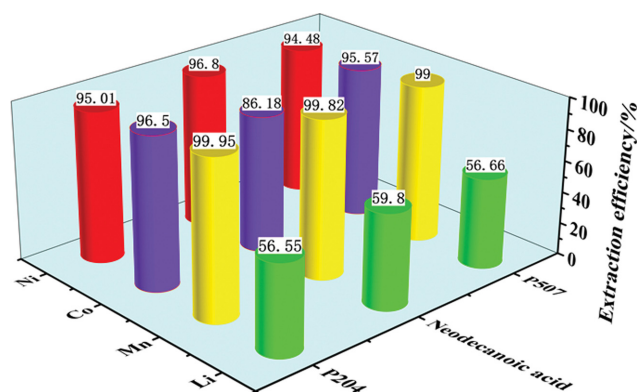


Fig. 2. Comparison of three extractants (50 vol% D2EHPA, extraction time 10 min, O/A=1, saponification percentage of 65%, room temperature).

lower than D2EHPA. The extraction efficiency of neodecanoic acid for nickel and manganese were both high, 96.8% and 99.82% respectively, but the extraction efficiency for cobalt was only 86.18%. Interestingly, the highest extraction efficiency for lithium was achieved by new decanoic acid (59.8%), followed by EHEHPA (56.66%) and D2EHPA (56.55%). EHEHPA is due to the weakening of the electronegativity of the ester oxygen atom in the molecule. As a result, its acidity was weaker than that of D2EHPA. Therefore, the distribution ratio of metal ions extracted by EHEHPA was lower than that of D2EHPA. Compared with D2EHPA and EHEHPA, neodecanoic acid has more steric hindrance effect, so the extraction selectivity of neodecanoic acid was better than D2EHPA and EHEHPA, especially the extraction selectivity for nickel and manganese was good. Therefore, the extraction ability of neodecanoic acid for cobalt was lower [29]. From the perspective of separation, the smaller the extraction efficiency of lithium ion is, the more favorable it is for separation. Therefore, D2EHPA is more suitable for the extraction separation of the studied system than the other two extraction agents.

Generally, the separation factor indicates the grade of separation and possibly separation occurs when separation factor >10 [23]. Table 2 shows the separation factors obtained with a single-stage extraction. The separation factors of nickel, cobalt, manganese and lithium ions, denoted by $\beta_{Ni/Li}$, $\beta_{Co/Li}$ and $\beta_{Mn/Li}$ respectively, were almost greater than 10 except for $\beta_{Co/Li}$ obtained during neodecanoic acid extraction. Moreover, the extractant with higher separation factors was D2EHPA, especially $\beta_{Mn/Li}$ used to indicate the separation grade of manganese and lithium ions.

2. Effect of Extractant Saponification Percentage on Extraction Performance

The effects of saponification percentage ranging from 30% to 85% [25] on the separation of manganese, cobalt, nickel and lith-

Table 2. Separation factors $\beta_{Me,i/Li}$ with different extractants (Me= Ni, Co or Mn)

Separation factor	$\beta_{Ni/Li}$	$\beta_{Co/Li}$	$\beta_{Mn/Li}$
D2EHPA	14.63	21.18	1,535.92
EHEHPA	13.09	16.50	75.73
Neodecanoic acid	20.34	4.19	372.79

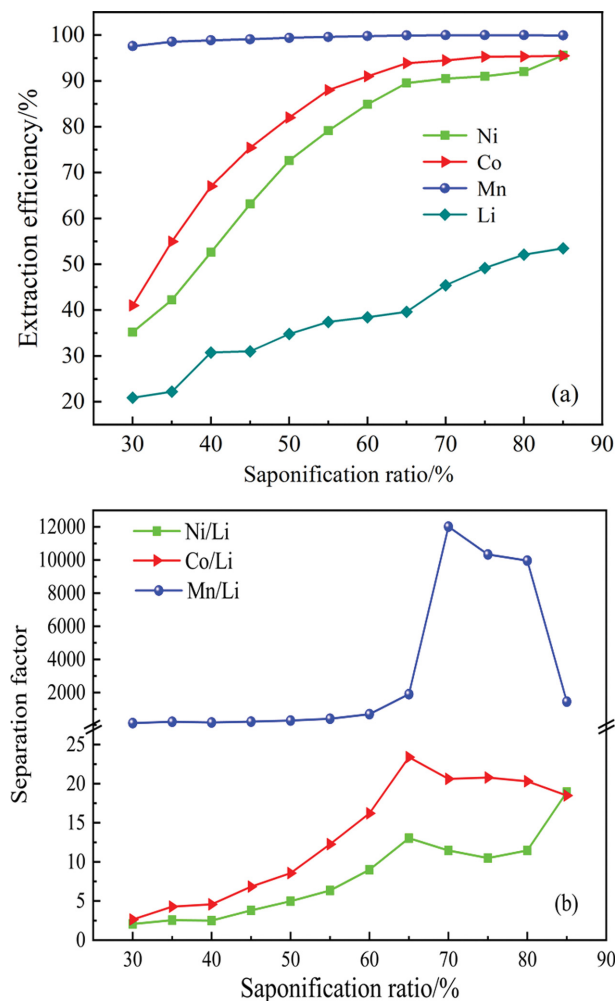
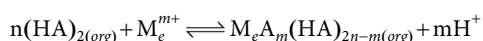


Fig. 3. Effect of saponification percentage on the extraction efficiency (a) and separation factor (b) (40 vol% D2EHPA, extraction time 10 min, O/A=1, room temperature).

ium ions are shown in Fig. 3 with fixed conditions of room temperature and D2EHPA volume content, extraction time, O:A phase ratio is 40%, 10 min, 1, respectively.

According to Fig. 3(a), it can be observed that the extraction efficiencies of metals (manganese, cobalt, nickel and lithium) increased with saponification percentage increasing. The extraction efficiency of nickel increased from 35.2% to 95.6%, the extraction efficiency of cobalt increased from 41% to 95.5%, the extraction efficiency of manganese increased from 97.6% to 99.94%, and the extraction efficiency of lithium increased from 20.89% to 53.46%. Using D2EHPA as the extractant, the reaction formula for extracting a metal ion is as follows [30]:



According to the reaction formula, the distribution ratio (D) can

be expressed as follows:

$$\log D = \log K + n \log [\text{HA}]_{(\text{org})} + m \text{pH}$$

The distribution ratio increases as the pH increases, and the higher valence state of the metal ions makes extraction easier [3]. The extraction efficiency or distribution ratio of different metal ions depends on three aspects: K, metal ion valence and pH value: K refers to the stability constant of the extraction complex formed by the metal ion and the organic part; pH, D are affected by pH and the magnitude of change is different. The extraction order of metal by D2EHPA is different under different pH values. At lower pH, D2EHPA can extract Mn^{2+} . And the higher valence state of the metal ions makes extraction easier [18]. When the saponification percentage is greater than 65%, the extraction efficiency of nickel, cobalt and manganese ions remains almost unchanged, while the extraction efficiency of lithium ions increases almost linearly. Therefore, the saponification percentage of D2EHPA should not exceed 65% in terms of lithium ions separation. As shown in Fig. 3(b), the separation factors also increase with the increase of saponification percentage when saponification percentage is no more than 65%. And the maximum value of separation factors $\beta_{\text{Ni/Li}}$, $\beta_{\text{Co/Li}}$ and $\beta_{\text{Mn/Li}}$ is 13.03, 23.42 and 1,904.24, respectively, which are all greater than 10. Further increasing saponification percentage of D2EHPA, the corresponding separation factor is also relatively large. Especially, when the saponification percentage increased to 70%, separation factor $\beta_{\text{Mn/Li}}$ reached more than 10^4 , which indicates that manganese and lithium ions can be separated quantitatively. However, separation factors $\beta_{\text{Ni/Li}}$ and $\beta_{\text{Co/Li}}$ both decreased due to the continuous increase of lithium ion extraction efficiency. Furthermore, the stronger the alkalinity of aqueous phase is, the greater the tendency of hydrolysis and polymerization of metal ions in solution shown. Since the metal ions after hydrolysis have hydrophilic groups, hydrolysis is not conducive to the extraction process. And when the degree of hydrolysis polymerization increases, it is easy to emulsify or form a third phase [16]. Hence, the appropriate saponification percentage is chosen to be 65% (At this time, the pH of the system is 4.93. The one-to-one correspondence between equilibrium pH and saponification percentage is shown in Table 3).

3. Effect of Extractant Volume Concentration on Extraction Performance

The saponification percentage of the fixed extractant was 65%, and the extraction was carried out at room temperature with O:A=1 and extraction oscillation time of 10 minutes. Excessive high concentration of extractant will increase the viscosity of organic phase and affect the rate of full mixing and full separating of the two phases, thus affecting the extraction and separation performance [31]. Therefore, the range of D2EHPA volume concentration investigated was set from 10% to 50%, and the influence of extractant concentration (v/v) on extraction is shown in Fig. 4.

As can be seen from Fig. 4(a), the extraction efficiency of nickel, cobalt, manganese and lithium ions all increase with the increase

Table 3. One-to-one correspondence between equilibrium pH and saponification percentage

Saponification percentage	30%	35%	40%	45%	50%	55%	60%	65%	70%	75%	80%	85%
pH	2.55	3.2	3.72	4.06	4.3	4.5	4.7	4.93	5.1	5.13	5.37	5.57

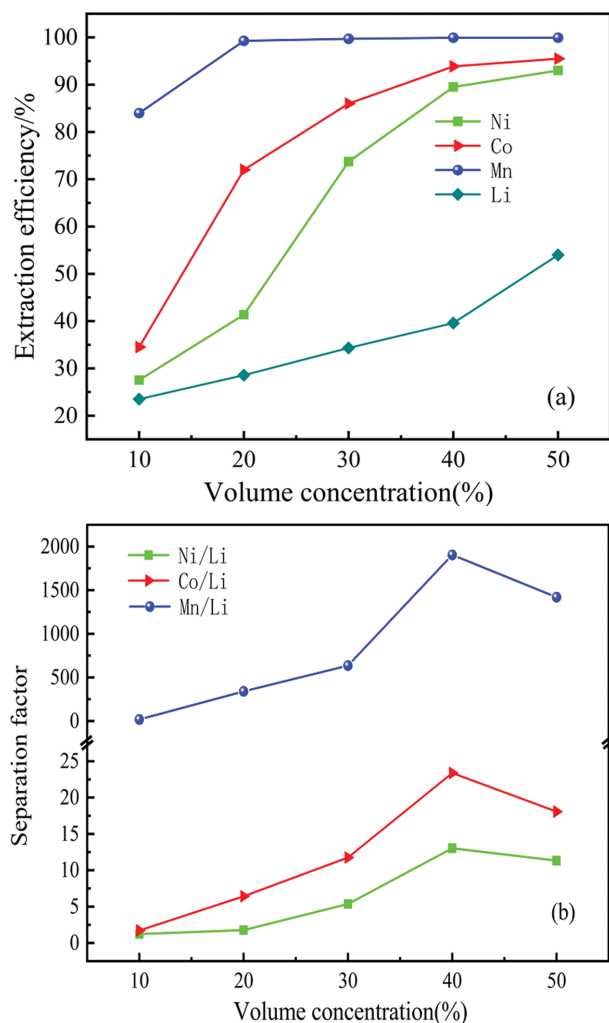


Fig. 4. Effect of % vol D2EHPA on the extraction efficiency (a) and separation factor (b) (extraction time 10 min, O/A=1, saponification percentage of 65%, room temperature).

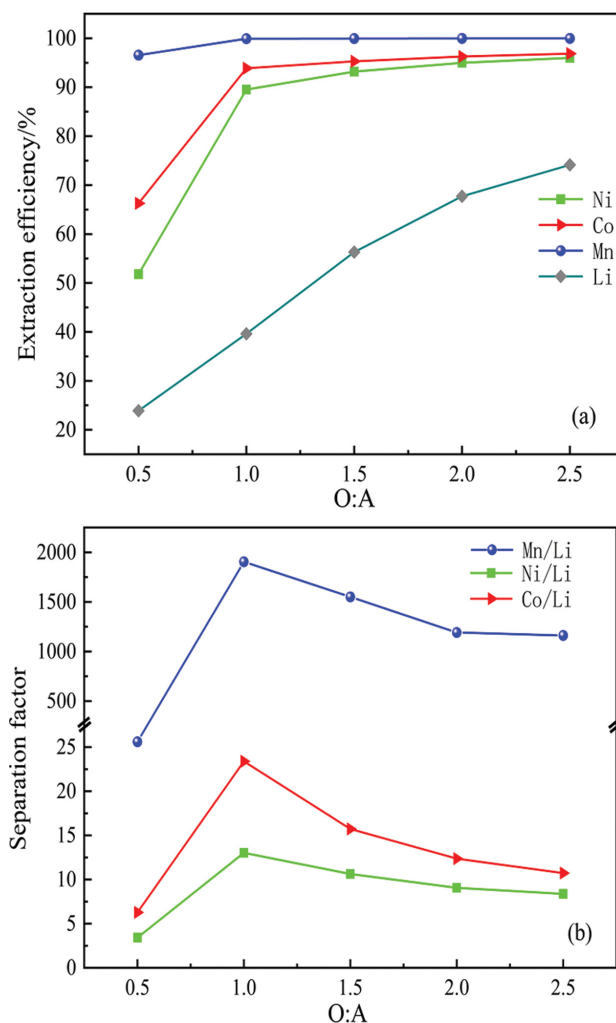


Fig. 5. Effect of O:A on the extraction efficiency (a) and separation factor (b) (extraction time 10 min, 40 vol% D2EHPA, saponification percentage of 65%, room temperature).

of the concentration of D2EHPA. When D2EHPA concentration is about 40%, the extraction efficiency of nickel, cobalt, and manganese reaches a higher value (Mn, 99.92%; Co, 93.88%; Ni, 89.52%) and does not change much with the further increase of extractant concentration. Consider the extraction selectivity and saturation capacity of D2EHPA, and the extraction capacity is related to the valence state of metal ions. When the value of n (metal valence) is high, D2EHPA can easily extract metal ions, so D2EHPA has a better extraction efficiency on nickel, cobalt and manganese. Therefore, extraction efficiency of lithium ions does not increase significantly with the increase of the extractant concentration, especially when D2EHPA concentration is lower than 40%. The relationship between separation factor and extractant concentration shown in Fig. 4(b) gives similar results. When D2EHPA volume concentration is 40%, the separation factors $\beta_{Ni/Li}=13.03$, $\beta_{Co/Li}=23.42$ and $\beta_{Mn/Li}=1,904.24$ all reached the maximum value in the extractant concentration range studied. Considering the separation effect of nickel, cobalt, manganese and lithium ions, the optimal concentration of D2EHPA was selected as 40% by volume.

4. Effect of Phase Ratio (O:A) on Extraction Performance

The effect of phase ratio (O:A) on extraction behavior was investigated under the conditions of D2EHPA volume concentration of 40%, saponification percentage of 65%, oscillation time of 10 min and room temperature; the results are presented in Fig. 5.

It can be seen from Fig. 5(a) that with the increase of O:A, the extraction efficiency of nickel increased from 51.79% to 96%, cobalt from 66.29% to 96.85%, and manganese from 96.56% to 99.96%, but the extraction efficiency of lithium also increased from 23.89% to 74.14%. When O:A was no larger than 1, there was a significant difference in the increase of extraction efficiency. Moreover, the extraction efficiency of nickel, cobalt and manganese ions was close to the extreme value under the given extractive condition. So, too high O:A is not conducive to the separation of lithium with nickel, cobalt and manganese. At the same time, too high O:A can cause water-in-oil or oil-in-water emulsion, resulting in loss of organic phase and higher cost [22]. When O:A=1, the extraction efficiency of cobalt and manganese ions was more than 90%, that of nickel ions was also close to 90%, and that of lithium ions was less than 40%.

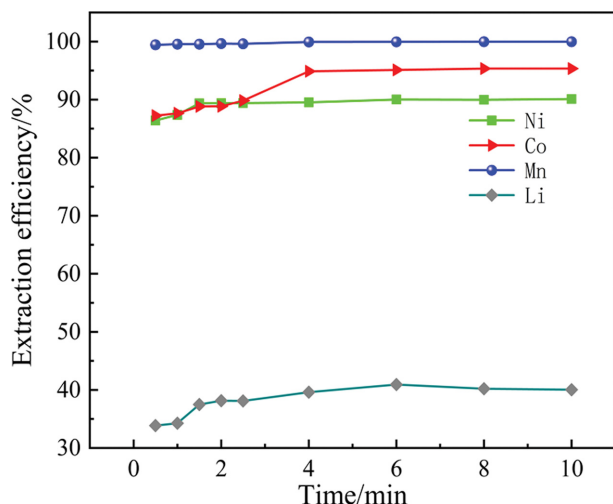


Fig. 6. Effect of extraction time on the extraction efficiency (40 vol% D2EHPA, O/A=1, saponification percentage of 65%, room temperature).

At the same time, as shown in Fig. 5(b), the three separation factors were all relatively large when O:A was 1 ($\beta_{Ni/Li}=13.03$, $\beta_{Co/Li}=23.42$ and $\beta_{Mn/Li}=1,904.24$). Hence, O:A of 1 was suitable to extraction.

5. Effect of Extraction Time on Extraction Performance

The effect of increasing extraction time from 0.5 to 10 min on extraction performance was investigated under the conditions of D2EHPA volume concentration of 40%, saponification percentage of 65%, room temperature and O:A of 1. The results are in Fig. 6.

The results show that when the extraction time was less than 4 minutes, the extraction efficiency of nickel, cobalt, manganese and lithium ions slightly increased and reached the maximum with the extension of the extraction time. It can be attributed to the fact that the extracting of these valuable metal cations with acidic extractant D2EHPA is essentially a proton exchange process, which can be expressed by Eq. (2). It is also evident from Fig. 6 that the extraction efficiency of manganese ions was very high, even of very short duration, indicating that manganese was the first to be extracted when extraction occurred and the stability constant of Mn extracted complex was the largest. The extraction of nickel and cobalt ions kept almost synchronous in the first 2.5 min of contacting time, but was out of sync as time continued to pass. The extraction efficiency of cobalt ions increased from 90% to 94% within 1.5 min of prolonged contacting time. However, the extraction efficiency of nickel ions remained almost unchanged, even if the contacting time was extended to 10 min. The extraction of lithium ions was basically completed within 1.5 minutes.

Three other kinds of metallic ions approached extraction equilibrium in about 4 minutes. The extraction time of 5 min was selected for subsequent experiments to ensure complete equilibrium. When the extraction time exceeded 5 min, the extraction efficiency of the four ions remained almost unchanged. Since the extraction process is a simple displacement reaction, the reaction process is not complicated. Therefore, to improve the separation efficiency of nickel, cobalt, manganese and lithium, the contacting time was chosen to be 5 minutes [32].

6. Determination of the Mathematical Model for the Extraction of Four Ions

The above experimental results showed that the volume concentration, O:A and saponification percentage of extractant D2EHPA all had effects on extraction performance. To understand the influence of other conditions on the extraction effects and make the study have guiding significance in industrial applications, we expanded the scope of influence factors investigated to carry out experiments, and correlated the results mathematically by the combined application of Levenberg-Marquardt method and Universal Global Optimization method, which would help to guide the practical extraction process influenced by multiple parameters. In this work, we correlated mathematically three parameters: distribution ratio (D), saponification percentage (Y) and volumetric fraction (X). With the influence range of variables determined, it should take into account that extractant D2EHPA at low concentration has the advantage of being easily mixed fully, quick phase splitting and high economic benefits [25,31]. Hence, a small concentration of extractant was selected and ranged 10%-50%. Data used to construct the model was obtained by variable-controlling approach and the specific test process was designed as follows: room temperature, O:A=1, certain oscillation frequency, contacting time of 5 minutes, 10%-80% saponification percentage of D2EHPA with 10%-50% volume concentration (both changed at an interval of 10%), the concentration of each metal ion in aqueous phase was determined and the distribution ratio of each metal ion was calculated, as shown in Table S1 (cf. Electronic Supplementary Material). A relational expression with distribution ratio as dependent variable and saponification percentage, volume concentration of extractant as independent variable was obtained by method of Levenberg-Marquardt and Universal Global Optimization. And according to formula (6), the final correlation equation of molar distribution ratio as dependent variable, O:A phase ratio, extractant saponification percentage and volume concentration as independent variable was obtained, which was applicable to an extractive process at low volume concentration extractant D2EHPA.

For Ni^{2+} , using Levenberg-Marquardt method and Universal Global Optimization method for calculation, the mathematical models of distribution ratio (D), saponification percentage (Y) and volume fraction (X) were obtained:

$$D = \frac{p_1 + p_2 * \ln X + p_3 * (\ln X)^2 + p_4 * Y + p_5 * Y^2 + p_6 * Y^3}{1 + p_7 * \ln X + p_8 * Y + p_9 * Y^2 + p_{10} * Y^3} \quad (R^2 = 0.992) \quad (5)$$

$$\text{And because, } D = \frac{n_o * V_a}{n_a * V_o} \quad (6)$$

Set the molar distribution ratio of certain metal ions in organic phase and water phase (n_o/n_a)= $D_{m, Mei}$ ($i=Ni^{2+}$, Co^{2+} , Mn^{2+} , Li^+), the volume ratio of water phase to organic phase (V_o/V_a)=(O:A),

$$D_{m, Ni} = \frac{a_1 + a_2 * \ln X + a_3 * (\ln X)^2 + a_4 * Y + a_5 * Y^2 + a_6 * Y^3}{1 + a_7 * \ln X + a_8 * Y + a_9 * Y^2 + a_{10} * Y^3} * (O:A) \quad (R^2 = 0.992) \quad (7)$$

Similarly, the extraction models of cobalt, manganese, and lith-

ium ions can also be obtained as Eqs. (8), (9), (10), respectively:

$$D_{m, Co} = \frac{b_1 + b_3 * X + b_5 * \ln Y + b_7 * X^2 + b_9 * (\ln Y)^2 + b_{11} * X * \ln Y}{1 + b_2 * X + b_4 * \ln Y + b_6 * X^2 + b_8 * (\ln Y)^2 + b_{10} * X * \ln Y} * (O:A) \quad (8)$$

($R^2 = 0.992$)

$$D_{m, Mn} = \frac{c_1 + c_2 * X + c_3 * X^2 + c_4 * c_{12} * \ln Y + c_5 * (c_{12} * \ln Y)^2 + c_6 * (c_{12} * \ln Y)^3}{1 + c_7 * X + c_8 * X^2 + c_9 * X^3 + c_{10} * c_{12} * \ln Y + c_{11} * (c_{12} * \ln Y)^2} * (O:A) \quad (9)$$

($R^2 = 0.999$)

$$D_{m, Li} = \frac{d_1 + d_2 * X + d_3 * X^2 + d_4 * Y + d_5 * Y^2 + d_6 * Y^3}{1 + d_7 * X + d_8 * X^2 + d_9 * Y + d_{10} * Y^2} * (O:A) \quad (10)$$

($R^2 = 0.98$)

The coefficients involved in the mathematical model are listed in Table 4.

To further verify the accuracy of the relational formula, the results obtained in the previous single-stage extraction experiments were compared with that obtained through the relation under the same extraction conditions (see Fig. 7).

For the mathematical model for extracting nickel ions, the comparison between the calculated and experimental data in Fig. 7(a)

Table 4. Coefficients

j	a_j	b_j	c_j	d_j
1	0.408	0.589	714.435	0.041
2	0.232	-3.824	3,740.367	0.132
3	0.059	8.178	2,408.879	0.115
4	-0.400	0.214	9,247.710	-0.507
5	-0.036	2.598	20,356.504	2.253
6	0.337	4.307	8,769.349	-1.897
7	-0.007	-3.518	138.602	-1.444
8	-4.124	1.115	-493.115	0.780
9	5.662	1.308	501.942	-0.21
10	-2.587	0.726	88.619	-0.264
11		2.574	197.439	
12			0.772	

shows that more than 80% of the data points are within the fitting error range of $\pm 15\%$. In Fig. 7(b) and Fig. 7(c), the mathematical model for cobalt and manganese extraction fits the experimental data to a higher degree. This may be because the three kinds of metal ions are extracted successively in sequence of manganese-

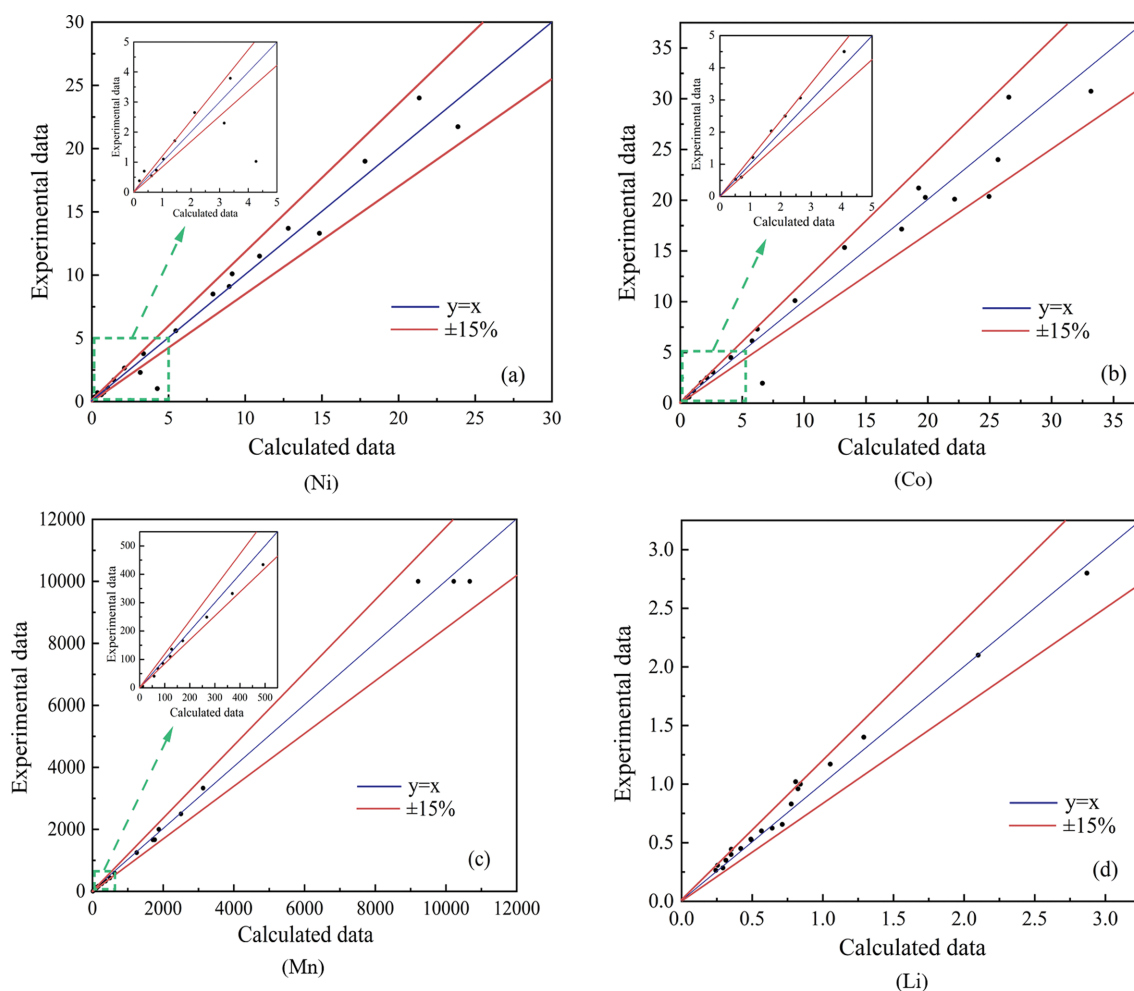


Fig. 7. Comparison chart of experimental data and calculated data.

cobalt-nickel, and the metal ions extracted later are greatly affected by the increase in the acidity of the extracted phase in such acid extraction system. In Fig. 7(a) and Fig. 7(b), when O:A ratio is as small as 0.5, the calculated data differs greatly from the experimental data, which can be attributed to an insufficient amount of extractant and the inability to extract multiple ions simultaneously. And the extractant preferentially extracts manganese ions, so the mathematical model for extracting nickel and cobalt at O:A=0.5 fits the experimental data to a lower degree. For the mathematical model for extracting lithium, as shown in Fig. 7(d), the fitting error between the calculated data and the experimental data is small. The ability of the acidic extractant (HA) to extract various metal ions (M^{n+}) is first determined by the stability constant β_n of the complex of M^{n+} and A^- . The larger the β_n , the more advantageous the extraction. The size of β_n is related to the valence (n) of metal ions. β_n of high-valent metal ions is larger than β_n of low-valent metals, so high-valent ions are easier to extract than low-valent ions. Therefore, when the four ions are extracted, lithium is finally extracted without being affected by other ions, so even when O:A=0.5, the deviation between the calculated data and the experimental value is not large.

CONCLUSIONS

We investigated a method to separate Co, Ni, Mn, and Li ions from synthetic leaching liquors of mixed cathode materials in spent lithium-ion batteries by solvent extraction. Through the single factor test in a single-stage extraction process, a more suitable extractant and better extractive condition was obtained. Among the three acidic extractants, D2EHPA was selected as the most suitable for the separation of Ni, Co, Mn and Li. In this process, Co, Ni and Mn are selectively extracted simultaneously, while a small amount of Li is co-extracted. The optimum separation factor values of a single stage extraction can be obtained under the conditions of extraction time 5 min, 40% volume concentration of D2EHPA, saponification percentage of 65%, O:A=1 and room temperature. And then almost 100% manganese, 94% cobalt and 90% nickel are co-extracted after a single-stage extraction.

Using Levenberg-Marquardt method and Universal Global Optimization method for correlating mathematically, the fitting degree of the extraction model and related parameters are determined. The functional relationship between the molar distribution ratio and extractant volume concentration, O:A, and saponification percentage in the system is obtained by function calculation. The model is validated by the comparison between the calculated and experimental data, which can be used as a guide for the extraction experiments in similar systems in the future.

ACKNOWLEDGEMENT

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

SUPPORTING INFORMATION

Additional information as noted in the text. This information is

available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

REFERENCES

1. T. Zhang, Y. He, F. Wang, L. Ge, X. Zhu and H. Li, *Waste Manag.*, **34**(6), 1051 (2014).
2. Y. Wang, L. Zeng, G. Zhang, W. Guan, Z. Sun, D. Zhang and J. Qing, *Hydrometallurgy*, **185**, 55 (2019).
3. Y. Yang, S. Lei, S. Song, W. Sun and L. Wang, *Waste Manag.*, **102**, 131 (2020).
4. Y. Yue, S. Wei, B. Yongjie, Z. Chenyang, S. Shaole and H. Yuehua, *ACS Sustain. Chem. Eng.*, **6**(8), 10445 (2018).
5. Y. Fu, Y. He, J. Li, L. Qu, Y. Yang, X. Guo and W. Xie, *J. Alloys Compd.*, **847**, 156489 (2020).
6. E. Quijada-Maldonado, F. Olea, R. Sepúlveda, J. Castillo, R. Cabezas, G. Merlet and J. Romero, *Sep. Purif. Technol.*, **251**, 117289 (2020).
7. J. Stefaniak, S. Karwacka, M. Janiszewska, A. Dutta, E. R. Rene and M. Regel-Rosocka, *Chemosphere*, **254**, 126869 (2020).
8. Y. Wang, H. Yang, G. Zhang, J. Kang and C. Wang, *Chem. Eng. J. Adv.*, **3**, 100023 (2020).
9. C. Liu, J. Lin, H. Cao, Y. Zhang and Z. Sun, *J. Cleaner Production*, **228**, 801 (2019).
10. J. Wang, J. Lu, M. Zhang, M. Tang, Q. Lu, Y. Qin, Y. Lu and B. Yu, *J. Hazard. Mater.*, **405**, 124211 (2021).
11. L. Xu, C. Chen and M.-L. Fu, *Hydrometallurgy*, **197**, 105439 (2020).
12. G. Zante, D. Trébouet and M. Boltoeva, *Appl. Geochem.*, **123**, 104783 (2020).
13. R. N. R. Sulaiman, N. F. M. Noah, N. Othman, N. Jusoh and M. B. Rosly, *Korean J. Chem. Eng.*, **38**(3), 514 (2021).
14. R. N. R. Sulaiman and N. Othman, *J. Hazard. Mater.*, **340**, 77 (2017).
15. Z. Li, X. Li, S. Raiguel and K. Binnemans, *Sep. Purif. Technol.*, **201**, 318 (2018).
16. L. Shuya, C. Yang, C. Xuefeng, S. Wei, W. Yaqing and Y. Yue, *Sep. Purif. Technol.*, **250**, 117258 (2020).
17. Q. Ye, G. Li, B. Deng, J. Luo, M. Rao, Z. Peng, Y. Zhang and T. Jiang, *Sep. Purif. Technol.*, **209**, 175 (2019).
18. Q. Sun, L. Yang, S. Huang, Z. Xu, Y. Li and W. Wang, *Miner. Eng.*, **132**, 284 (2019).
19. M. T. Coll, A. Fortuny, C. S. Kedari and A. M. Sastre, *Hydrometallurgy*, **125-126**, 24 (2012).
20. R. Torkaman, M. Asadollahzadeh, M. Torab-Mostaedi and M. Ghanadi Maragheh, *Sep. Purif. Technol.*, **186**, 318 (2017).
21. M. J. Jung, P. Venkateswaran and Y. S. Lee, *J. Ind. Eng. Chem.*, **14**(1), 110 (2008).
22. J. Chen, *Handbook of hydrometallurgy*, Metallurgical industry Press, Beijing (2005).
23. S.-H. Joo, S. M. Shin, D. Shin, C. Oh and J.-P. Wang, *Hydrometallurgy*, **156**, 136 (2015).
24. W. Chu, Y. Zhang, X. Chen, Y. Huang, H. Cui, M. Wang and J. Wang, *J. Power Sources*, **449**, 227567 (2020).
25. Y. Yang, S. Xu and Y. He, *Waste Manag.*, **64**, 219 (2017).
26. S. Virolainen, M. Fallah Fini, A. Laitinen and T. Sainio, *Sep. Purif. Technol.*, **179**, 274 (2017).
27. T. Liu, J. Chen, H. Li and K. Li, *Sep. Purif. Technol.*, **245**, 116869 (2020).

28. L. Wang, Y. Wang, L. Cui, J. Gao, Y. Guo and F. Cheng, *Sep. Purif. Technol.*, **251**, 117371 (2020).
29. A. J. M. Santanilla, P. Aliprandini, J. Benvenuti, J. A. S. Tenorio and D. C. R. Espinosa, *Miner. Eng.*, **160**, 106691 (2021).
30. D. Shi, B. Cui, L. Li, M. Xu, Y. Zhang, X. Peng, L. Zhang, F. Song and L. Ji, *Desalination*, **479**, 114306 (2020).
31. H. Wang, Y. Feng, H. Li, H. Li and H. Wu, *Hydrometallurgy*, **195**, 105404 (2020).
32. H.-F. Li, L.-J. Li and W. Li, *Chem. Phys. Lett.*, **754**, 137675 (2020).

Supporting Information

Separation of valuable metals from mixed cathode materials of spent lithium-ion batteries by single-stage extraction

Yongjie Li, Qiang Fu, Hongyun Qin, Kun Yang, Junnan Lv, Qicheng Zhang, Hui Zhang, Feng Liu, Xia Chen[†], and Ming Wang[†]

School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo 255049, China
(Received 26 January 2021 • Revised 26 April 2021 • Accepted 3 May 2021)

Table S1. Distribution ratio of each elemental under different conditions

Volume concentration	Saponification percentage	D _{Ni}	D _{Co}	D _{Mn}	D _{Li}
0.1	0.1	0.191	0.058	0.775	0.060
0.2	0.1	0.225	0.079	1.335	0.062
0.3	0.1	0.352	0.197	2.142	0.106
0.4	0.1	0.420	0.242	3.077	0.135
0.5	0.1	0.440	0.247	4.395	0.236
0.1	0.2	0.216	0.108	0.986	0.046
0.2	0.2	0.234	0.149	2.122	0.080
0.3	0.2	0.240	0.158	4.60373	0.085
0.4	0.2	0.322	0.316	13.969	0.135
0.5	0.2	0.440	0.468	25.830	0.294
0.1	0.3	0.220	0.104	1.312	0.038
0.2	0.3	0.351	0.159	4.558	0.057
0.3	0.3	0.610	0.339	19.463	0.094
0.4	0.3	0.830	0.839	59.040	0.210
0.5	0.3	1.376	1.514	99.167	0.413
0.1	0.4	0.392	0.167	1.887	0.103
0.2	0.4	0.443	0.387	15.243	0.239
0.3	0.4	0.627	0.976	60.32653	0.306
0.4	0.4	1.156	2.325	142.095	0.438
0.5	0.4	1.924	4.093	260.304	0.503
0.1	0.5	0.434	0.260	2.913	0.231
0.2	0.5	0.623	0.881	30.632	0.263
0.3	0.5	1.100	2.190	92.906	0.380
0.4	0.5	1.470	2.548	170.714	0.444
0.5	0.5	1.560	3.050	186.812	0.556
0.1	0.6	0.472	0.381	4.319	0.228
0.2	0.6	0.766	1.549	45.231	0.309
0.3	0.6	1.800	3.859	124.208	0.436
0.4	0.6	6.240	10.652	157.158	0.681
0.5	0.6	10.000	14.714	374.625	0.953
0.1	0.7	0.434	0.459	5.254	0.231
0.2	0.7	0.922	2.846	59.1	0.326
0.3	0.7	2.840	7.160	299.5	0.509
0.4	0.7	8.970	17.581	6,009	0.803
0.5	0.7	17.049	25.190	6,009	1.208
0.1	0.8	0.472	0.902	10.693	0.233799
0.2	0.8	1.351	4.140	88.701	0.345109
0.3	0.8	4.870	10.364	600	0.586538
0.4	0.8	11.443	24.943	6,009	0.780576
0.5	0.8	20.260	32.951	6,009	1.475