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The Extraction Behavior of Acidic Phosphorus-Containing Compounds to Some Metal Ions: A Combination Research of Experimental and Theoretical

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Abstract

In order to provide feasible methods for the extraction of valuable metals from spent batteries or low-grade primary ores, the extraction behavior of some representative acidic phosphorus-containing compounds (APCC) as extractants is evaluated from the perspective of experimental and theoretical investigations in this work. Aqueous solutions containing five metal ions, Ca(II), Co(II), Mg(II), Mn(II), and Ni(II), were made to simulate leaching liquids, and the extraction of these metals were investigated. A simplified calculated model was used to evaluate the interaction between each extractant and metal ions. The calculation results agree well with the experimental tests in trend. This work not only provides potential extractants for the extraction of valuable metals from spent batteries or low-grade primary ores, but also demonstrates the practicability of the simplified calculation model.

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1. Introduction

According to a report from Bloomberg New Energy Finance, the NCM (nickel, cobalt, manganese) ternary battery production capacity in 2019 reached 229 GWh, taking up 69% of the entire Li-ion battery production capacity, and the NCM production capacity keeps increasing rapidly. In the EV(Electric Vehicle) battery industry, NCM battery adoption rate constantly increases and is expected to increase from 45% in 2018 to 64% in 2025.[1] Namely, various hybrid electric, pure electric, and plug-in hybrid electric vehicles have occupied an increasing market in society, which directly results in the increasing demand for related metals and the urgent need for the treatment of solid waste of spent batteries. Addressing these issues would lay a solid foundation for the continuous developing of EV battery industry. However, the high-grade ores, such as copper-nickel sulphide, have been exhausting, and the low-grade ores, such as laterite, gradually become the one important resource.[2-3] Under the context of sustainable development and environmental production,[4] the cost of traditional treatment, transportation, and storage of solid waste are becoming expensive rapidly. Consequently, in the foreseeable future, the resources of metal raw materials used for batteries are mainly low-grade ores, and, especially, spent batteries.[5] One of the common important characters of the low-grade ores and spent batteries is that both of them contain more calcium and magnesium, but less cobalt, nickel, manganese. Therefore, efficient separation of metals is of significant importance.[6-7] The popular separation methods include resin ion exchange,[8] electrochemical method,[9-10] selective precipitation,[11-12] bio-hydrometallurgy,[13] solvent extraction,[14-18] and the combination of some above methods.[12] Compared to other methods, solvent extraction is quite attractive due to simple and convenient operations, high efficiency, excellent selectivity and high capacity.

Solvent extraction in hydrometallurgy is an efficient method for recycling, separation, and purification of metals to obtain highly pure metals, such as rare-earth elements,[19-20] actinides,[21-22] transition metals,[18,23-24] alkali metals,[14] and alkaline metals.[25-26] In laboratory, the solvent extraction of general metal ions includes the following steps, the preparation of aqueous metal-ion solutions and organic extractant solutions, the extraction of metal ions from the aqueous solutions by organic solutions, the measurement of the concentration of metal ions in both phases and the measurement of pH value in aqueous phase, and the final analysis of the experimental data.[27-28] The solvent extraction strategy has found widespread application in the recycling of spent batteries and the refining of low-grade ores.[7] For instance, a recycling approach containing mechanical pre-treatment and solvent extraction operations developed by Granata et al., which could accomplish the European Guideline 2006/66/EC for recycling of nickel metal hydride, lithium ion, and primary lithium batteries.[17] And, the recovery of manganese from a solution containing cobalt, nickel, and lithium, leached from spent lithium-ion battery ternary cathodic material, was achieved by Joo et al..[29] More related researches on the extraction and separation of metal ions have been collected in recent reviews.[16,27,30] These reports demonstrate that the solvent extraction is a potential efficient approach to solve the separation problem.

In the solvent extraction process, the selected extractant is very important. It determines almost all extraction operation parameters, such as acidity, concentration, stages, stripping, etc., and also decides the total efficiency of the extraction process.[16,29,31] As versatile extractants, acidic phosphorus-containing compounds (APCC) have been widely used in hydrometallurgy.[28,32-33] Some commercial available APCC extractants include bis(2-ethylhexyl) phosphate (P204), 2-ethylhexyl (2-ethylhexyl)phosphonate (P507), bis(2-ethylhexyl)phosphinic acid (P227), bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272, or C272).[18,34-40] In order to obtain efficient extractants, extensive studies on the design and QSPR (quantitative structure-property relationship) of APCC have been performed. Yuan et al. showed that the Hammett constants, the Taft constants, the number of infrared spectroscopies, acidic dissociation constants, and electronic density (calculated with Hückel molecular orbital) on oxygen are directly related to the extraction abilities of APCC.[41-43] A novel

APCC extractant, USTB-2, designed by Wang et al., was found to be a superior extractant, compared with the commercial available Cyanex 272, for the extraction and separation of rare-earths.[44] Additionally, the extraction of valuable metals from spent batteries or low-grade ores by APCC has also been explored.[17,29,31] For instance, Ichlas et al. reported the Cyanex 272 could directly extract the nickel and cobalt from the nitric acid leaching solution of laterite ores.[18] These reports indicated that the APCC have enormous potential application in extraction of valuable metals from spent batteries or low-grade ores.

Although a number of APCC have been studied in academic areas and used in industrials,[33,45] the extraction and separation properties of various APCC have not been investigated systemically. Furthermore, according to the “9S rule” proposed by professor Yuan,[46] the popular extractants usually exhibit some inferior characteristics, such as low capacity, low selectivity, and high stripping acidity. Therefore, it is still highly desirable to develop more efficient extractants. We have previously developed an approach to evaluate the QSPR for the separation and extraction of several trivalent lanthanide ions by APCC from the theoretical and experimental point of view,[47-48] various APCC were synthesized and characterized, and their extraction and separation properties under different condition were also tested. And the first-stability constants were used to simulate the overall extraction equilibrium constants in trend. Compared to the completely coordinated model by using excessive extractants,[49] our model by using 1 equiv of extractant can save the computer resource significantly, which is favorable for the calculation of the interaction between extractants and metal ions with a great reliability. Additionally, the varied conformations in the model would not be a significant calculation issue because only one-molecule residue of the extractant existed surrounding the metal ions.[30,50]

Since APCC may have great potential in the extraction and separation of valuable metal ions from spent batteries and low-grade ores,[27] in this work we continuously focus on the extraction properties of some representative APCC for the extraction and separation of five metal ions, Ca(II), Co(II), Mg(II), Mn(II), and Ni(II). Some other metal ions, including Al(III), Cu(II), Fe(III), Li(I) and Na(I) are also common components of leaching liquid obtained from spent batteries or low-grade ores.[7,51-54] Al(III), Cu(II) and Fe(III) ions can be easily removed by proper pretreatment before the extraction process. The Fe(III) ion may be removed by precipitation,[5], the Al(III) ion can be excluded via the formation of AlO_2^-, and the Cu(II) ion can be extracted with Acorga M5640.[55] Usually, Li(I) and Na(I) ions would stay in the aqueous solution when extracted by APCC. Based on these facts, only the above five metal ions are considered here. Firstly, the extraction behavior of six APCC, P1C6, P127, P118, P208, P227, and P2361 to the above five metal ions was investigated, and the first-stability constants were also computed in order to examine the reliability of the simplified model on the evaluation and prediction of the extraction and separation properties of the six APCC. Secondly, the extraction properties of two commercially available extractants, Cyanex 272 and P507, for the extraction and separation of the above five metal ions is predicted by the simplified calculated model, and then the prediction results were verified by experimental evidence. This work provides potential extractants for the separation of Ca(II), Co(II), Mg(II), Mn(II), and Ni(II) metal ions, explains general principles of the interaction between extractants and metal ions, and offers an approach for the prediction of extraction efficiency.

2. Experiment and computation sections

2.1 Experimental details

Materials

The APCC, P1C6, P127, P118, P208, P227, and P2361 (di(cyclohexyl)phosphinic acid, di(1-ethylhexyl)phosphinic acid, di(1-methylheptyl)phosphinic acid, di(2-methylheptyl)phosphinic acid, di(2-ethylhexyl)phosphinic acid, and di(2-isopropylpentyl)phosphinic acid, respectively), were synthesized according to our previous reports.[47-48] $NaH_2PO_2{\cdot}H_2O$ (20 mmol), acetic acid

(20 mmol), alkene (42 mmol), di-t-butyl peroxide (DTBP; 8 mmol), and dimethylformamide (10 mL) were placed in a 50-mL autoclave. The mixture was stirred at 130 °C for 10 h. The solvent was removed under reduced pressure. The residue was dissolved in water, acidified with HCl, and extracted with diethyl ether. The ether layer was washed with water and the solvent was evaporated. Into the residue was added NaOH (1 mol/L) until pH = 7, and diethyl ether was added to dissolve some organic impurities. The residue was heated under vacuum at 100 °C to give APCC in about 87% yield. The Cyanex 272 and P507 were purchased from AoDa chemical without further purification. Other reagents used in this work were analytical pure.

Extraction process

In order to determine the influence of operation conditions on the extraction and separation efficiency, we have conducted some extraction experiments under different conditions, such as varying diluents, extractant concentrations, extraction temperatures and shaking time. In all experiments, aqueous sulfate solutions of the metal ions (Ca(II), Co(II), Mg(II), Mn(II), and Ni(II)) were prepared by diluting metal sulphates to 0.002 mol/L with deionized water. Sodium sulfate was used to maintain the ionic strength in aqueous phase. An APCC solution and an aqueous metal sulfate solution (equal volume with APCC solution) were mixed together and the resulting mixture was kept shaking at 300 rpm in a separating funnel fixed on a thermostatic oscillator. The concentrations of metal ions in each phase were analyzed by ICP (SPECTRO ARCOSFHS12), and the pH values of two aqueous were measured by pH meter (PHS-3E).

2.2 Computational details

Model

As reported in literature, the extraction chemical equation of M^{n+} (M^{n+} is Ni(II), Co(II), Mn(II), Ca(II), and Mg(II)) with APCC (HA is P1C6, P127, P118, P208, P227, and P2361) could be represented as:[15,29,56]

$$nH_2A_{2(o)} + M^{n+}_{(aq)} \rightarrow M(HA_2)_{n(o)} + nH^+_{(aq)} \qquad \Delta G_{EX}, K_{EX} \tag{1}$$

where, the ΔG_{EX} and K_{EX} refer to the difference of Gibbs free energy and the corresponding extraction equilibrium constants for the extraction chemical reaction, respectively. H_2A_2 refers to the dimer of HA. According to various reports,[28,57-58] these compounds prefer to dimerize in diluent solutions.[57,59] The subscripts, (o) and (aq) refer to organic and aqueous phase, respectively. Because $M(HA_2)_n$ contains over two hundred atoms and a large number of different conformations may exist, it is not easy to optimize their molecular structures accurately.[49] Namely, the ΔG_{EX} and K_{EX} are difficult to calculate. Consequently, in previous reports,[47-48] a simplified chemical reaction,

$$1/2H_2A_{2(o)} + M^{n+}_{(aq)} \rightarrow MA^{(n-1)+}_{(o)} + H^+_{(aq)} \qquad \Delta G_{EX,1}, K_{EX,1} \tag{2}$$

was proposed to qualitatively estimate the ΔG_{EX} and K_{EX}. Where, the $\Delta G_{EX,1}$ and $K_{EX,1}$ refers to the difference of Gibbs free energy when the first ligand coordinated on the metal center in the extraction process, and the $K_{EX,1}$ refers to the corresponding first equilibrium constant. As indicated in our previous reports, the $\Delta G_{EX,1}$ and $K_{EX,1}$ calculated from density functional theory share the same trend with ΔG_{EX} and K_{EX} tested from the experimental approach.[47-48] Therefore, the $\Delta G_{EX,1}$ is also applied to estimate the ΔG_{EX} too in trend in this work, as shown as Figure 1. The distorted conformation was adopted for the ligand in $[Co(H_2O)_5A]^+_{(o)}$ in order to reflect the steric effect of alkyl group in extractants, especially the α- or β-substituted alkyl group.[47-48] The $[M(H_2O)_6]^{2+}$ was used to represent the forms of aqueous metal ions, Ni(II), Co(II), Mn(II), and Mg(II).[60-61] In the case of Ca(II), $[Ca(H_2O)_7]^{2+}$ was found to be the hydrated form.[62-63] The dimeric forms were adopted for all APCC.[48,59] Tetramer of water and hydrion ion hydrated by four molecules of water were adopted according to literatures.[64-67] The extraction process is replacing the coordinated waters by the anion of extractant.[68]

Calculation

All geometries were fully optimized without any restriction at the DFT (density functional theory) B3PW91 theory level,[69] and the vibrational frequencies were calculated to ensure all structures were located on the minimal point of potential surface. The solvent effect was included by using the SMD solvation model,[70] considering water and *n*-dodecane as the aqueous and organic phases, respectively, and using a single-point calculation based on the optimized structures. The conformations with the lowest energies were used if multiple possible conformations existed. In these calculations, the 6-31+G*[71] basis set was used for C, H, O, P, and Mg, and the LANL2DZ was used for Ni, Co, Mn, and Ca.[72] All calculations were performed in Gaussian 09 software package.[73]

3. Results and discussion

3.1 The extraction efficiency under different operation conditions

The influence of operation conditions, such as varying diluents, extractant concentrations, extraction temperatures and shaking times, on the extraction efficiency has been evaluated initially by using the P227 as an extractant, the results are collected in Table 1.

As listed in the Table 1, the pH value at 50% extraction rate (pH^{50}) for the extraction of the five metal ions by P227 under different operating conditions are collected. Three concentrations of P227, 0.05, 0.20, and 0.50 mol/L were considered. The pH^{50} values clearly indicated that the organic phase with higher concentration of extractants can extract metal ions with more efficiency[28,57] and would lead to lower pH^{50} . The concentration of extraction almost did not affect the order of pH^{50}, except Ca(II) and Mg(II). We also considered the temperatures of 10, 25, and 40 °C, the shaking times of 5, 15, 30, 60 min, and the use of *n*-dodecane, sulfonated kerosene, toluene, and E100 (a commercial solvent, a mixture of alkane) as diluents. The pH^{50} values were slightly affected by the above operating conditions. The shorter shaking times and higher temperatures led to higher pH^{50}, but the type of diluents had little influence on the pH^{50} values. However, the order of pH^{50} were almost not changed, except the Ca(II) and Mg(II). These facts demonstrated that the operation conditions can impact the extractability of organic phases, but has little influence on the separability of the organic phases. The separability is a key issue in extracting metals from low-grade primary ores or spent batteries. And in the following sections, we concentrated on the separability under specific conditions, i.e., 0.20 mol/L concentration of APCC in *n*-dodecane, shaking time of 30 min, and operating temperature of 25 °C.

3.2 The extraction behavior observed by experimental tests

In order to present the extraction and separation properties of APCC, P1C6, P127, P118, P208, P227, and P2361 for the extraction of Ni(II), Co(II), Mn(II), Ca(II), and Mg(II)metal ions, the extraction rates at different acidity were tested as declared in 2.1 section, the plots of extraction rates versus equilibrium aqueous pH values were plotted in Figure 2, and pH^{50} (the pH values when extraction rate was 50%) were collected in Table 2.

As shown in Figure 2, the extraction rates of each metal ion by each APCC increased with extraction equilibrium pH value increasing when no precipitate was formed. This is a general phenomenon observed frequently in acidic extraction system.[16,29,31,45] However, these six APCC showed largely different extraction behaviors. Firstly, the compounds containing bulkier alkyl groups (such as P1C6 and P127, Figure 2a and 2b) led to the formation of metal-complex precipitates at lower pH. Low extraction rate was observed by using these compounds as extractants, especially for the extraction of Ni(II) and Ca(II). The extraction rate of Ni(II) and Ca(II) by P1C6 was lower than 10% at pH < 5 and emulsions were formed at pH > 5. In contrast, P118 and P208, containing smaller substituents, showed superior extraction properties and even at pH > 6.5 no emulsion or precipitation was formed (Figure 2c and 2d). This agree well with Guimarães' reports that the crud would be formed at pH ≈ 6.[31] The bulky-substituent effects could be ascribed to some facts. Firstly, the steric hindrance reduces the coordination ability of the phosphoryl oxygen. Without the coordination to the extractants, metal ions may easily undergo hydrolysis to form precipitations. Secondly, the compounds containing larger substituents exhibited lower solubility, which results in lower saturation capacity and would easily lead to the formation of emulsion.[74-78]

In a solution containing the five metal ions, it is important to determine the separation ability of each APCC. As shown in Figure 2, the separation ability of each APCC is reflected by the distance between different lines under the same pH-value conditions. The larger the distance is, the better the separation ability is. The six APCC have very different separation ability. For instance, P127(Figure 2b), could separate Mn(II) and Co(II) from Mg(II), Ca(II), and Ni(II) at pH=4-5, but P2361(Figure 2f) could not. Similarity, P118 (Figure 2c) could separate Ni(II) from other ions at pH=5. Although all of the APCC have the same core structure, $R_2P(O)OH$ (R = alkyl group), Figures 2a-2f clearly show that slight modifications of the alkyl substituents led to significant changes in the extraction priority. The positions of the blue and black lines, reflecting the extraction rates of Mg(II) and Ca(II), respectively, changed significantly in the six pictures, suggesting that the presence of Mg(II) and Ca(II) ions would increase the difficulty in the separation of Ni(II), Co(II), and Mn(II) ions.[79]

In order to reveal the metal-ion extraction priority order, the pH^{50} were collected in Table 2. As listed in Table 2, the values of pH^{50} are affected not only by the acidic dissociation constants (pK_a) of extractants, but also by the nature of metal ions, especial their hydrolysis characteristics.[80] Usually, extractants with lower pK_a value would exhibit stronger extractability.[28,37] Although pK_a (5.36) of P1C6 is lower than that of P2361 (pK_a = 5.80), their pH^{50} values for the extraction of Ca(II) are 5.51 and 4.57, respectively, meaning that P2361 shows stronger extractability. A similar case was found for the extraction of Mn(II) by these two APCC. Obviously, both extractant and metal ions together determine the order of pH^{50}. In other words, neither of these two factors can solely determine the extraction and separation properties. Therefore, the extraction of the same metal ion from different mixtures may require the use of a different extractant. For the separation of a metal-ion mixture by an extractant, the larger the difference between pH^{50} is, the higher efficiency the separation can achieve. As shown in Table 2, the pH^{50} of Co(II) and Ni(II) are 4.15 and 6.73, respectively, by using P208 as the extractant. their difference between these two pH^{50} value is 2.58, and the difference is 1.48 by using P2361 as the extractant. Clearly, P208 is more efficient than P2361 for the separation of Co(II) from Ni(II). Based on the pH^{50} listed in Table 2, it is easy to choose an appropriate extractant for the separation of selected ion mixtures.

3.3 Evaluating the extraction behavior from computational calculations.

It is clear that the alkyl substituents are important in metal ion extraction.[47-48,81] In order to deeply understand the interaction between metal ions and extractants and to explain the influence of alkyl substituents, a simplified extraction model was calculated with the density functional theory as described in section 2.2. The results were listed in Table 3.

As shown in Table 3, $\Delta G_{EX,1}$ reflects the extraction priority order of different metal ions. By using the same APCC, the larger the difference of $\Delta G_{EX,1}$ is, the higher efficiency the separation process can achieve. Furthermore, the relative difference of $\Delta G_{EX,1}$ between two ions by using the same APCC also agrees well with the relative difference of pH^{50}. These results indicated that our previous simplified calculation model proposed for the extraction of lanthanide ions could be applied to evaluate the extraction of other metal ions.[47-48] Moreover, the same conclusion could be drawn that the P208 is more efficient than P227 for the separation of Ni(II) from the mixture of Co(II) and Mn(II) ions, as $\Delta G_{\mathrm{EX},1}$ between Ni(II) and Co(II)/Mn(II) is larger by using P208 than that by using P2361.

With this simplified model in hand, further calculation was performed for two commercial extractants, C272 and P507, and the results were also collected in the bottom layer of Table 3. The prediction of separation ability of C272 and P507 for the separation Ni(II) and Co(II) agree well with the experimental results obtained by Sarangi et al..[28] Our calculation results indicated that the separation order is C272 > P507 > P227, and the differences of $\Delta G_{\mathrm{EX},1}$ between Ni(II) and Co(II) are 25.95, 18.70, and 16.75 $\mathrm{kJ \cdot mol^{-1}}$ for C272, P507, and P227 respectively.

Table 2 and 3 provides much valuable information for the extraction of some metal ions by APCC. For instance, some APCC (P208, P1C6, etc.) have higher selectivity than the commercial extractants, C272 and P507, for the separation of Co(II)/Ni(II). Both Table 2 and 3 indicated that the alkyl substituents are the critical factors to determine the extraction and separation behaviors of APCC.[47-48] In fact, the alkyl substituents are the only differences in the structures of these APCC, and the slight differences result in the significantly different extraction behaviors, especially the separation abilities. The extraction characteristics are partially determined by the acidity of extractants, but acidity is not an only factor. according to Liu's opinion, acidity is a local property of molecules.[82] Since the conformations of alkyl substituents has little influence on the inductive effects of coordination atoms in extractants, the conformations of alkyl substituents would have little effect on the acidity of extractants, meaning that the interaction strength between metal ions and coordination center would not be influenced by the conformations of alkyl groups. But the orientations of alkyl chains could affect the coordination of other ligands, and thus the distorted conformations were used in the simplified calculation model. These results indicated that the simplified model could successfully simulate complicated complexes if proper distorted conformations are used.

4. Conclusion

In this work, the extraction behavior of several APCC (P1C6, P127, P118, P208, P227, and P2361) for the extraction of metal ions (Ni(II), Co(II), Mn(II), Ca(II), and Mg(II)) were revealed from the perspective of experimental and theoretical investigations. The experimental results indicated that the APCC have great potential for the extraction of the above metal ions from leaching liquids obtained from spent batteries or primary ores, some of them (e.g. P208, P1C6) have superior selectivity than commercial extractants (P507, C272, etc.) for the extraction of some metal ions, such as Co(II) and Ni(II), and the separability is not sensitive to the operation conditions. A simplified calculation model with only one equiv of extractant considered was used to understand the interaction between extractants and metal ions from the theoretical perspective. The consistence of computational calculation with experimental results indicated that the simplified model could provide a convenient approach for the prediction of extraction efficiency.

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Notes
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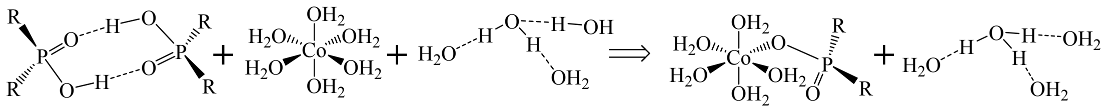


$$\mathbf{1/2}\ H_2A_{2(o)} + [Co(H_2O)_6]^{2+}_{(aq)} + \mathbf{3/4}\ (H_2O)_{4(aq)} \longrightarrow [Co(H_2O)_5A]^{+}_{(o)} + H^{+}(H_2O)_{4(aq)}$$

Figure 1. The proposed first extraction step. The Co(II) was used as the example. The Ni(II), Mn(II), and Mg(II) share the same form of Co(II), but the $[Ca(H_2O)_7]^{2+}$ and $[Ca(H_2O)_6A]^{+}$ were used for Ca(II).

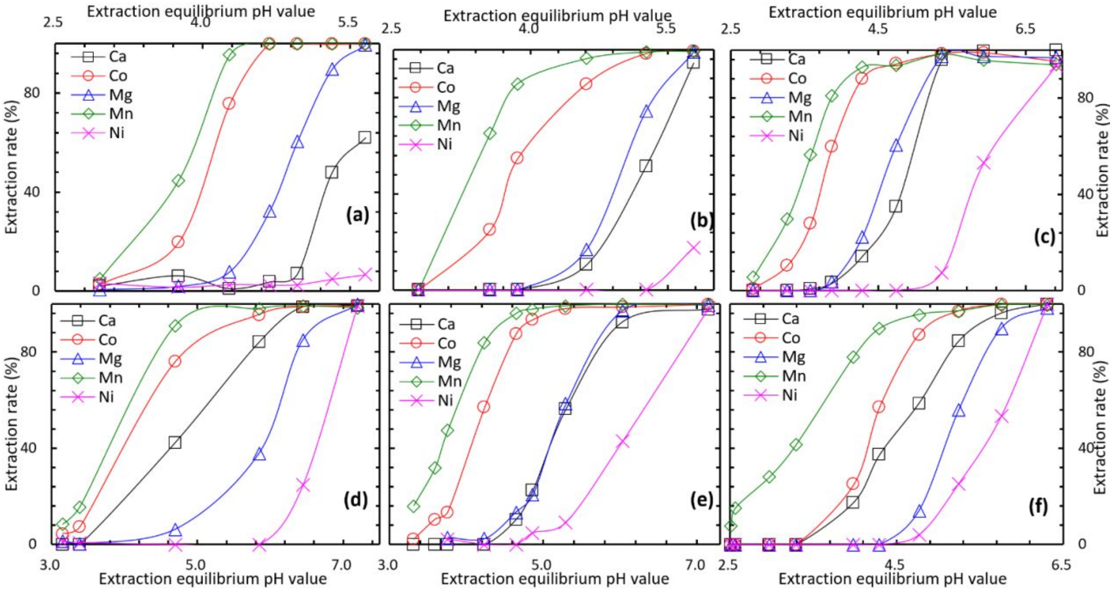


Figure 2. The extraction rate of different metal ions Ca(II), Co(II), Mg(II), Mn(II), and Ni(II) at various equilibrium pH values. The (a), (b), (c), (d), (e), and (f) correspond to P1C6, P127, P118, P208, P227, and P2361.

Table 1. The pH value at 50% extraction rate (pH^{50}) of P227 to the five metal ions under different operation condition.

c(mol/L)	*T*(°C)	*t*(min)	Diluent	Ca(II)	Co(II)	Mg(II)	Mn(II)	Ni(II)	The order of pH^{50}
0.05	25	30	*n*-Dodecane	5.23	4.23	5.25	3.90	6.25	Mn<Co<Ca≈Mg<Ni
0.20	25	30	*n*-Dodecane	5.20	4.16	5.18	3.79	6.18	Mn<Co<Mg≈Ca<Ni
0.50	25	30	*n*-Dodecane	4.93	4.03	5.07	3.60	5.97	Mn<Co<Ca<Mg<Ni
0.20	25	60	*n*-Dodecane	5.19	4.13	5.18	3.77	6.19	Mn<Co<Mg≈Ca<Ni
0.20	25	15	*n*-Dodecane	5.23	4.20	5.25	3.80	6.21	Mn<Co<Mg≈Ca<Ni
0.20	25	5	*n*-Dodecane	5.32	4.30	5.36	3.83	6.41	Mn<Co<Mg≈Ca<Ni
0.20	10	30	*n*-Dodecane	5.20	4.20	5.33	4.10	6.35	Mn<Co<Ca<Mg<Ni
0.20	40	30	*n*-Dodecane	5.30	4.30	5.50	4.40	6.70	Mn<Co<Ca<Mg<Ni
0.20	25	30	Sulfonated Kerosene	5.33	4.18	5.20	3.71	6.13	Mn<Co<Mg<Ca<Ni
0.20	25	30	Toluene	5.40	4.28	5.29	3.88	6.30	Mn<Co<Mg<Ca<Ni
0.20	25	30	E110	5.25	4.22	5.14	3.85	6.22	Mn<Co<Mg<Ca<Ni

Table 2. The pH^{50} of different APCC to various metal ions.

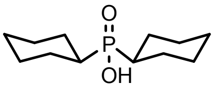
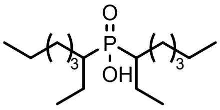
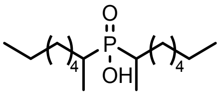
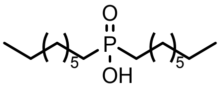
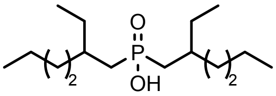
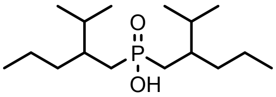
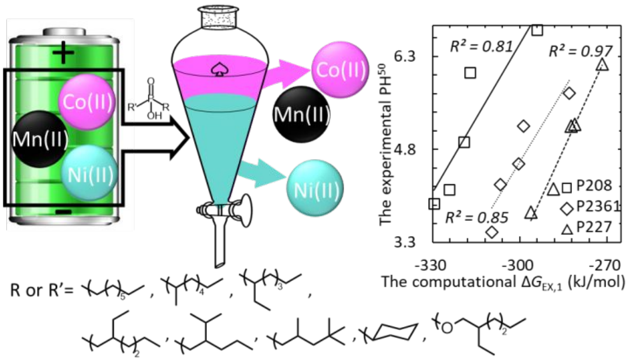
name	pK_a	Structure	Ca(II)	Co(II)	Mg(II)	Mn(II)	Ni(II)	The order of pH^{50}
P1C6	5.36		5.51	3.83	4.87	3.59	>5.6	Mn<Co<Mg<Ca<Ni
P127	5.82		5.24	3.78	5.00	3.37	>5.8	Mn<Co<Mg<Ca<Ni
P118	5.42		4.91	3.88	4.62	3.52	5.88	Mn<Co<Mg<Ca<Ni
P208	4.96		4.92	4.15	6.04	3.93	6.73	Mn<Co<Ca<Mg<Ni
P227	5.60		5.20	4.16	5.18	3.79	6.18	Mn<Co<Mg≈Ca<Ni
P2361	5.80		4.57	4.23	5.18	3.46	5.71	Mn<Co<Ca<Mg<Ni

Table 3. The difference of Gibbs free energies of the simplified extraction reaction $\Delta G_{EX,1}$ (kJ·mol^{-1}). The pH^{50} of Cyanex 272 (C272) and P507 were also tested and collected for comparation.

	APCC	Ca(II)	Co(II)	Mg(II)	Mn(II)	Ni(II)	The order of $\Delta G_{EX,1}$
Training	P1C6	-298.70	-301.02	-300.36	-302.31	-269.64	Mn<Co<Mg<Ca<Ni
	P127	-272.05	-285.11	-276.57	-288.83	-267.55	Mn<Co<Mg<Ca<Ni
	P118	-284.30	-296.59	-284.48	-301.86	-274.53	Mn<Co<Mg≈Ca<Ni
	P208	-319.22	-324.36	-317.17	-329.46	-294.15	Mn<Co<Ca<Mg<Ni
	P227	-281.10	-288.32	-282.41	-296.20	-271.57	Mn<Co<Mg<Ca<Ni
	P2361	-300.34	-306.76	-298.62	-309.70	-282.97	Mn<Co<Ca<Mg<Ni
Test	C272	-306.27	-301.79	-304.03	-308.62	-275.84	Mn<Ca<Mg<Co<Ni
		4.97	4.29	5.06	3.99	6.13	Mn<Co<Ca<Mg<Ni
	P507	-297.42	-296.92	-295.79	-298.58	-278.22	Mn<Ca<Co<Mg<Ni
		3.21	3.88	4.45	3.10	5.37	Mn<Ca<Co<Mg<Ni

TOC Graphic


Co(II)
Mn(II)
Ni(II)
R or R'=
The experimental PH50
The computational $\Delta G_{EX,1}$ (kJ/mol)
R² = 0.81
R² = 0.97
R² = 0.85
P208
P2361
P227
6.3
4.8
3.3
-330
-300
-270