

## Article

# Distinct Extraction Behaviors of La/Ce and Sc/Y in the Phosphoric Acidic Leachate of Bauxite Residues and Their Sequential Extraction with Di-(2-Ethylhexyl) Phosphoric Acid as Extractant

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**Abstract:** Bauxite residue is a hazardous solid waste produced in the alumina production process and has also become a significant rare earth resource. The extraction behaviors of La, Ce, Sc and Y solubilized in the phosphoric acidic leachate of bauxite residue were investigated in this study with di-(2-ethylhexyl) phosphoric acid as the extractant. With a relatively low concentration of 2% at an aqueous solution pH of 1.5, 90% Sc and 98% Y were extracted by di-(2-ethylhexyl) phosphoric acid. Less than 5% La and Ce and impurities of Fe, Al, Ti and Ca were extracted in this situation. As the concentration of di-(2-ethylhexyl) phosphoric acid increased to 20%, almost all the Sc and Y were extracted and the extraction ratios of La and Ce were 87% and 95%, respectively. A good separation of REEs against impurities was simultaneously obtained in the solvent extraction process and their separation coefficients were much higher than 1. A stepwise extraction process was proposed and established to extract Sc/Y and La/Ce sequentially from the phosphoric acidic leachate. It was further revealed that the Sc and Y in the acidic leachate were extracted by di-(2-ethylhexyl) phosphoric acid through an ion exchange process, and that the extraction of La and Ce was due to an antagonistic process where both an ion exchange reaction and a solvation reaction occurred.

**Keywords:** rare earth; bauxite residue; phosphoric acid; solvent extraction; di-(2-ethylhexyl) phosphoric acid; solid waste utilization; hydrometallurgy



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## 1. Introduction

Bauxite residue is a hazardous solid waste mainly produced in alumina refinery processes and has an adverse effect on the surrounding environment, primarily due to its high alkalinity [1–3]. Approximately 160 million tons of bauxite residues are generated annually in the world [4] and the efficient utilization of bauxite residues has been a huge challenge confronting the alumina industry. A variety of valuable components, including iron, alumina, titanium, and multiple rare earth elements (REEs), co-exist in bauxite residues and mean that bauxite residues have become an important secondary resource [5,6]. The extraction of the valuable components in bauxite residues has attracted much attention across the world and is considered to be an effective means of achieving the value-added utilization of bauxite residues.

The REEs contained in bauxite residues are at a content of 500–1700 mg/kg [7,8], and the primary REEs are lanthanum(La), cerium(Ce), neodymium(Nd), praseodymium(Pr), scandium(Sc), and yttrium(Y) [9]. Bauxite residues have provided potential opportunities for the production of REEs apart from the use of ion adsorption clay deposits [10]. The REEs in bauxite residues are generally extracted through acid leaching followed by a solvent extraction process. The conventionally used acids HCl [11], H<sub>2</sub>SO<sub>4</sub> [12,13], HNO<sub>3</sub> [14]

are widely adopted in the acid leaching process for the dissolution of REEs. Recently, phosphoric acid [15] was also utilized for Sc leaching from bauxite residues.

However, it has been shown that the components of iron, alumina, and silica in bauxite residues are also easily dissolved in the acid solution along with REEs, and, furthermore, cause emulsification in the following solvent extraction process for REEs, dramatically decreasing the yields of REEs. Therefore, some pretreatments before acid leaching to separate these dominant components in bauxite residues are often conducted for REEs extraction. Smelting reduction [16] and reductive roasting [17] followed by magnetic separation were proved to be efficient techniques for the recovery of iron in bauxite residues, and alkali roasting proved effective to extract alumina and obtain good separation against REEs [18]. Silica was found to be the most unfavorable impurity for REEs extraction. A dry-digestion process was also applied to avoid the co-dissolution of silica with REEs in bauxite residues, achieving excellent separation of REEs over silica [19,20].

The solvent extraction process has been widely used to extract solubilized REEs in the acid leachate of bauxite residues due to its simplicity, rapidity, and applicability over various concentration ranges [21]. The organic extractants of neutral phosphorus [22,23], acidic phosphorus [23–25], carboxylic acids [26], and amines [27,28] have been intensively utilized in practical production for REEs extraction, which were exhibited in Table 1. Acidic phosphorus extractants were demonstrated to be the most commercial and have been widely applied. Di-(2-ethylhexyl) phosphoric acid (P204) is one of the typical acidic phosphorus extractants used for the extraction of REEs. It has invariably been used to extract the REEs in the acidic leachate of bauxite residues treated with HCl, HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> [29–31].

**Table 1.** The common extractants for REEs extraction.

Kind of Extractant	Typical Extractants	Medium	Complication on REEs
neutral phosphorus	CYANEX 925 [22], TBP [23]	HCl H <sub>2</sub> SO <sub>4</sub>	La, Y Ce
acidic phosphorus	Cyanex 272, Cyanex 572 [24] D2EHPA [25]	HNO <sub>3</sub> HCl	La, Y, Nd Sc
carboxylic acids	PC-88A [26]	HCl	Dy, Nd
amines	Aliquat 336 [27] N1923 [28]	HNO <sub>3</sub> HCl	Y Th, U

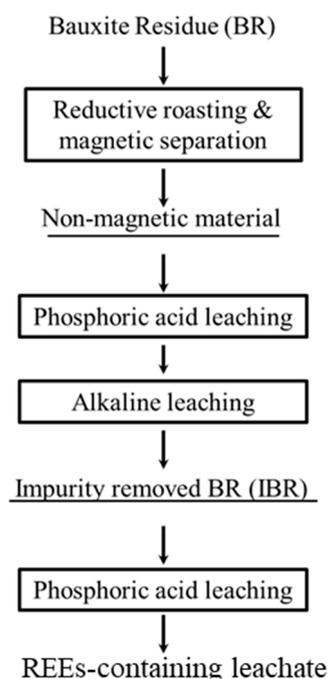
In our previous work, phosphoric acid was introduced to dissolve REEs and to simultaneously obtain good recovery of TiO<sub>2</sub> in impurity-removed bauxite residues (IBR) [32], in which the iron, alumina, and silica in the bauxite residue had already been stepwise extracted through a reductive roasting and magnetic separation process followed by a two-step leaching process [33,34]. The excellent performance of saponified P204 for the separation of Sc from the phosphoric acidic leachate of bauxite residues has also been demonstrated [35]. Since multiple REEs of La, Ce, and Y, as well as of Sc, were contained in the bauxite residues, the observation of the extraction of these multiple REEs with P204 was of great significance. Furthermore, the saponification of P204 would result in increased water pollution, so the extraction of the REEs with non-saponified P204 is preferred.

In this study, P204 without saponification was proposed to be used for the extraction of the multiple REEs La, Ce, Sc, and Y in the phosphoric acidic leachate of bauxite residues, and the extraction behaviors of La, Ce, Sc, and Y were intensively investigated under various concentrations of P204 and aqueous solution pH values. The performances of the major impurities of Fe, Al, Ti, and Ca in the phosphoric acid leachate were also examined and the optimal conditions for the separation of the REEs from impurities were examined. Furthermore, the mechanism for the extraction of the multiple REEs of La, Ce, Sc, and Y in the phosphoric acid leachate with P204 was ascertained.

## 2. Materials and Methods

### 2.1. Materials

The acidic leachates containing the REEs in this study were obtained through leaching an impurity-removed bauxite residue (IBR) with phosphoric acid liquor. The flow chart for obtaining the REEs-containing phosphoric acid solution from the bauxite residue was shown in Figure 1.



**Figure 1.** Flow chart for obtaining the REEs-containing phosphoric acid solution from the bauxite residue.

The chemical composition and phase compositions of the original bauxite residue (BR) and the IBR are shown in Table 2 and Figure 2, respectively. Based on our previous work [32–34], the IBR used in this study was collected after optimized reductive roasting at 1100 °C with sodium additives and magnetic separation with 0.1T, followed by continuous leaching with 1.2 mol/L phosphoric acid at 40 °C and 35 wt.%. NaOH liquor at 260 °C was subsequently applied to the BR. More than 90% of the dominant components of iron, silica, and alumina were successively separated after this process. The main REEs of La<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub>, Sc<sub>2</sub>O<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub> in the BR were dramatically enriched in the IBR. The concentrations attained were 0.0491 wt.%, 0.237 wt.%, 0.038 wt.%, and 0.0745 wt.%, respectively, enriched by about four times compared with the BR.

**Table 2.** Main chemical compositions of the bauxite residues (wt.%).

	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Na <sub>2</sub> O	CaO	TiO <sub>2</sub>	La <sub>2</sub> O <sub>3</sub>	Ce <sub>2</sub> O <sub>3</sub>	Sc <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	LOI
BR	31.6	18.7	12.2	6.6	13.3	5.2	0.0117	0.0534	0.0086	0.0178	12.0
IBR	3.4	2.0	1.8	14.1	28.0	22.3	0.0491	0.237	0.038	0.0745	22.3

BR: Bauxite residue; IBR: impurity-removed bauxite residues; LOI: loss on ignition.

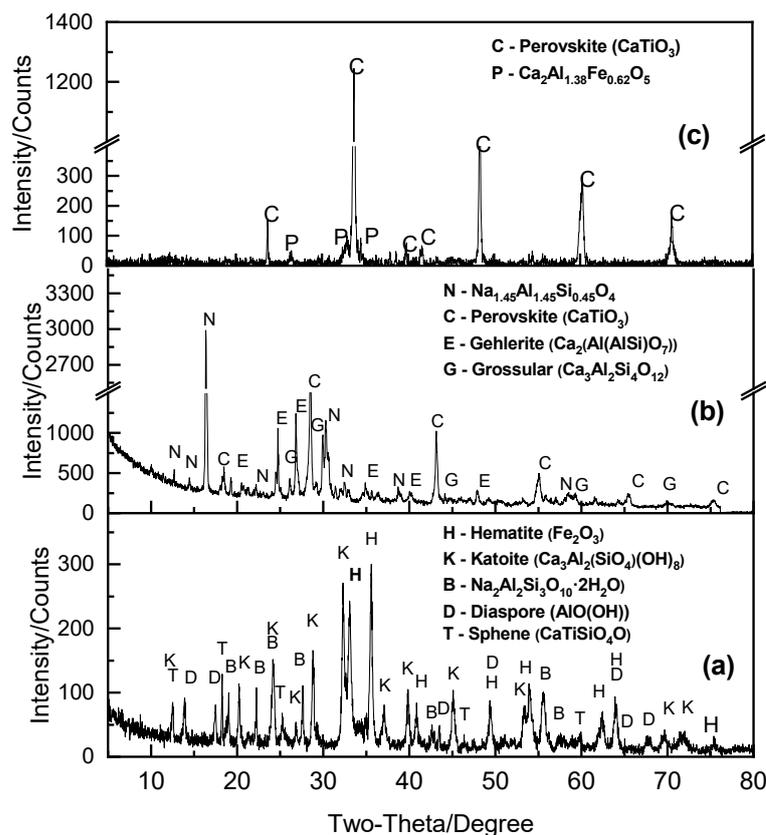


Figure 2. XRD patterns of BR (a), non-magnetic material (b), and IBR (c).

The X-ray diffraction patterns (XRD) indicated that the diffraction peaks of hematite in the BR disappeared in the non-magnetic material after the reductive roasting and magnetic separation process. The Al- and Si-bearing minerals in the BR were dehydrated and further transformed into sodium aluminosilicates, grossular, and gehlenite in the non-magnetic material, as shown in Figure 2b. At the same time, a new mineral of perovskite was formed in the non-magnetic material. As a two-step leaching process was further conducted on the non-magnetic material, most of the Al- and Si-bearing minerals were dissolved, and their diffraction peaks disappeared in the leached residue, namely the IBR. The XRD patterns indicated that the IBR mainly comprised perovskite, as shown in Figure 2c.

A phosphoric acidic leaching process was subsequently conducted on the IBR with an acid concentration of 10 mol/L, a liquid-to-solid ratio of 10, a leaching time of 60 min, and a leaching temperature of 150 °C. A total of 90% of the REEs in the IBR was effectively solubilized and 98% TiO<sub>2</sub> was reserved in the leached residues. The concentration of the REEs and the dominant impurities are shown in Table 3. It can be seen that the contents of the dominant impurities of Fe, Al and Ti were still higher than that of the REEs in the phosphoric acidic leachate despite most of them having already been removed in the up-stream processes. The observation of the separation of the REEs against impurities in the solvent extraction, resulting in a high yield of REEs, is of great significance.

Table 3. Concentration of rare earth and dominant impurities in phosphoric acidic leachate (mg·L<sup>-1</sup>).

La.	Ce	Sc	Y	Al	Fe	Ti	Ca
33.5	100.3	15.5	26.3	1690	2136	820	10,470.8

## 2.2. Methods

### 2.2.1. Procedure of the Solvent Extraction Process

In this experiment, P204 was used to selectively extract REEs in the diluted phosphoric acidic leachate of IBR without saponification to reduce ammonia pollution. Kerosene was utilized as a diluent to configure the P204 at different concentrations. The solvent extraction process was conducted at ambient temperature with an aqueous-to-organic ratio of 3 and an extraction time of 15 min based on previous investigation. Moreover, it was found that white precipitates were formed when the initial aqueous solution pH was adjusted above 2.3; the highest pH of the acidic leachate was, therefore, controlled at about 2.0. The initial pH value of the acidic leachate was approximately 0.5.

At the beginning of the solvent extraction experiment, the prepared P204 and the leachate were sequentially added into a 125 mL pear-shaped separator funnel, such that their sum did not exceed one third of the total volume of the funnel. A glass piston was then inserted into the mouth of the funnel to seal it completely. Following this, the separator funnel was placed in a gas bath oscillator at room temperature. The funnel was shaken uniformly for a period of time when the oscillation program was turned on. After the shaking was completed, the separator funnel was taken out and was left to stand still for the separation of the organic phase and the aqueous phase. Subsequently, the organic phase and the aqueous phase were released successively from the lower end of the funnel. The contents of the rare earth elements and the impurities in the diluted solution were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Thermo Fisher Scientific, Icap7400 Radial, USA).

### 2.2.2. Indexes in the Solvent Extraction Process

The recovery ratio ( $\eta$ ) of the rare earth metal and the impurity in the solvent extraction process was calculated based on the variation in their contents in the acidic solution after the solvent extraction process, according to Equation (1).

$$\eta = \left(1 - \frac{C_1 \cdot V_1}{C_0 \cdot V_0}\right) \times 100 \quad (1)$$

where  $C_0$  and  $V_0$  refer to the element content in the original leachate and the volume of the acidic leachate before the solvent extraction process, and  $C_1$  and  $V_1$  refer to the element content and the volume of the aqueous phase after the solvent extraction process. Generally, the  $V_0$  is equal to  $V_1$ .

The distribution ratio ( $D$ ) refers to the ratio of the total concentration of an element in the organic phase to its total concentration in the aqueous phase after the solvent extraction process reaches equilibrium, which is calculated according to Equation (2).

$$D = \frac{C_0 \cdot V_0 - C_1 \cdot V_1}{C_1 \cdot V_2} \quad (2)$$

where  $V_2$  refers to the volume of the organic phase.

The separation coefficient ( $\beta$ ) characterizes the separation difficulty of the REEs against impurities in the solvent extraction process. It is calculated based on the distribution ratio of the rare earth and impurity element in the solvent extraction process, according to Equation (3).

$$\beta_{(A/B)} = \frac{D_A}{D_B} \quad (3)$$

where  $D_A$  refers to the distribution ratio of the rare earth element, such as La, Ce, Sc, or Y, and  $D_B$  represents the distribution ratio of the impurity element, such as Fe, Al, Ti, and Ca.

### 2.2.3. Test Techniques

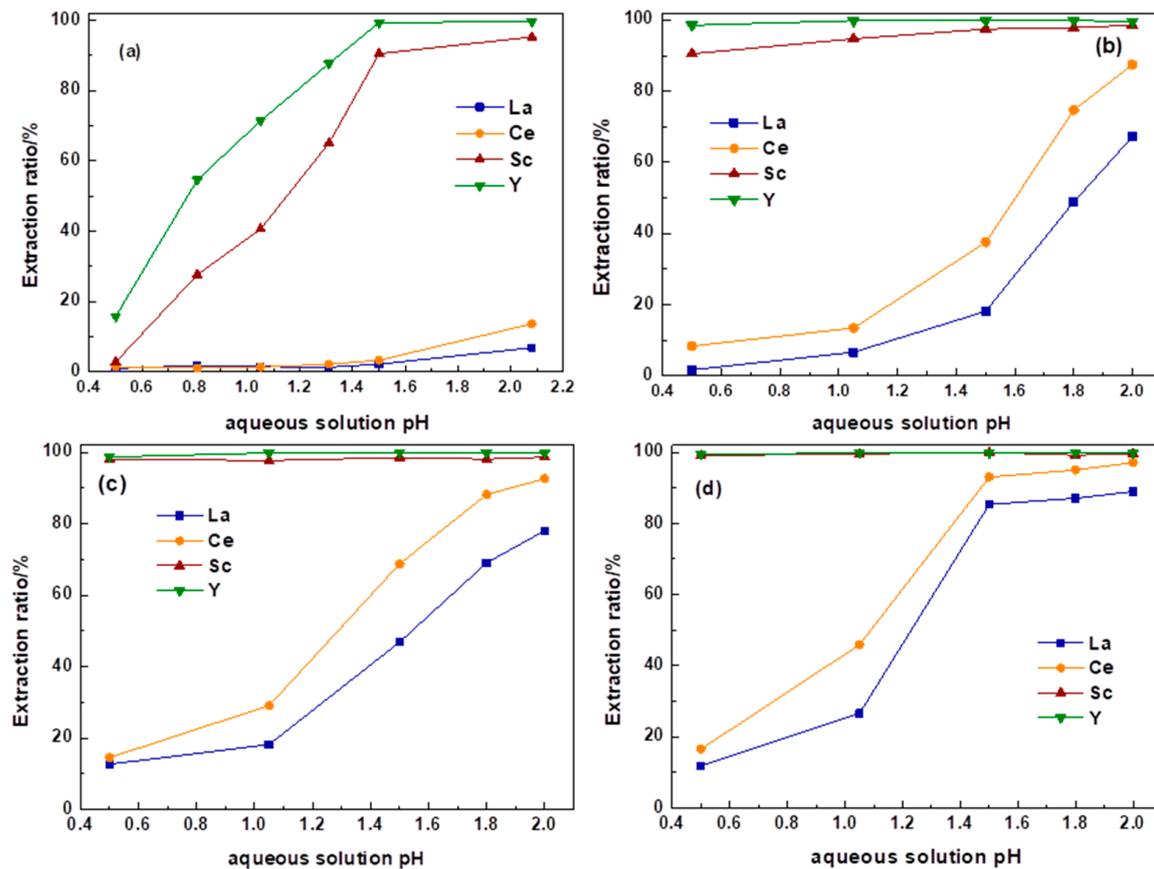
The dominant chemical compositions of the bauxite residues were determined using an X-ray fluorescence spectrometer (XRF, PANalytical, Axios mAX, Almelo, The Netherlands).

The contents of the trace rare earth elements in the bauxite residue were ascertained using a plasma emission spectrometer (ICP-AES, Thermo Fisher Scientific, Icap7400 Radial, Waltham, MA, USA), which was applied after the solid sample was completely solubilized.

### 3. Results and Discussion

#### 3.1. Extraction Behaviors of Various REEs in the Phosphoric Acidic Leachate

The behaviors of La, Ce, Sc, and Y at various concentrations of P204 and initial pH values of the solution were studied; the results are shown in Figure 3.



**Figure 3.** Extraction behaviors of the rare earth elements La, Ce, Sc, and Y at various concentrations of P204 and aqueous solution pH values: (a) 2% P204; (b) 10% P204; (c) 15% P204; (d) 20% P204.

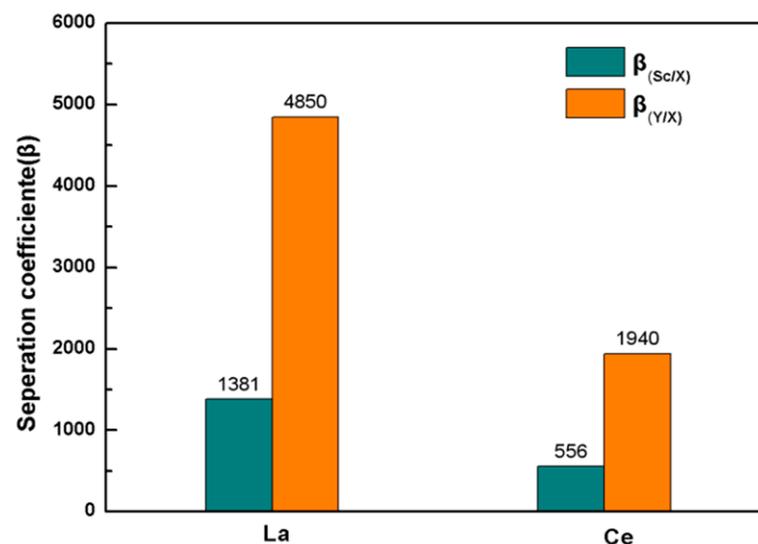
In Figure 3a, it can be seen that the extraction ratios of Sc and Y increased rapidly when the initial solution pH was raised and the concentration of P204 was 2%. The extraction ratios were only 2.8% and 15.9%, respectively, at an initial solution pH of 0.5, but were about 90% and 98%, respectively, at solution pH of 1.5, while both attained 98% at solution pH of 2.0. As the concentration of P204 increased to 10%, as shown in Figure 3b, the extraction ratios of Sc and Y were approximately 90% and 98%, respectively, at an initial solution pH of 0.5. The extraction ratio of Sc rapidly increased to 98% when the solution pH was raised to 1.5. Further increase in the P204 concentration did not increase the extraction ratio of Sc and Y as they had already reached the maximum value of 98%. The results are shown in Figure 3c,d.

At the same time, it was observed that La and Ce exhibited distinct behaviors compared with Sc and Y. As can be seen in Figure 3a, limited quantities of La and Ce were extracted over the course of the experiment and their extraction ratios were basically lower than 10% as P204 was at a low concentration of 2%. The extraction ratios started to increase gradually with increase in the concentration of P204. The aqueous solution pH was also beneficial for the extraction of La and Ce, as shown in Figure 3b–d. Inferior extraction of La

and Ce occurred when the concentration of P204 was less than 15%, with the extraction ratios being less than 80%, even at a high solution pH of 2.0. Optimal extraction of La and Ce was obtained when the concentration of P204 was 20% at pH above 1.5. The extraction ratios of La and Ce reached about 87% and 95%, respectively, at solution pH of 1.5, and further increased to 92% and 98% at solution pH of 2.0.

These results indicate that the REEs of La, Ce, Sc, and Y in the phosphoric acidic leachate of bauxite residues can be sequentially extracted through different concentrations of P204 at appropriate initial solution pH values. A low concentration of P204 at 2% is sufficient to achieve the extraction of Sc and Y when the solution pH is about 1.5, and a higher concentration of P204 at 20% can be utilized to extract La and Ce. A stepwise extraction process is, thus, recommended for the sequential extraction of Sc/Y and La/Ce.

The separation coefficients of Sc/Y against La/Ce at a P204 concentration of 2% and an initial pH value of 1.5 were calculated; the results are shown in Figure 4. The separation coefficients of Sc against La and Ce were 1381 and 556, respectively, while the values for Y against La and Ce attained 4850 and 1940. The results validate the prior extraction of Sc/Y using P204 at low concentration of 2%.

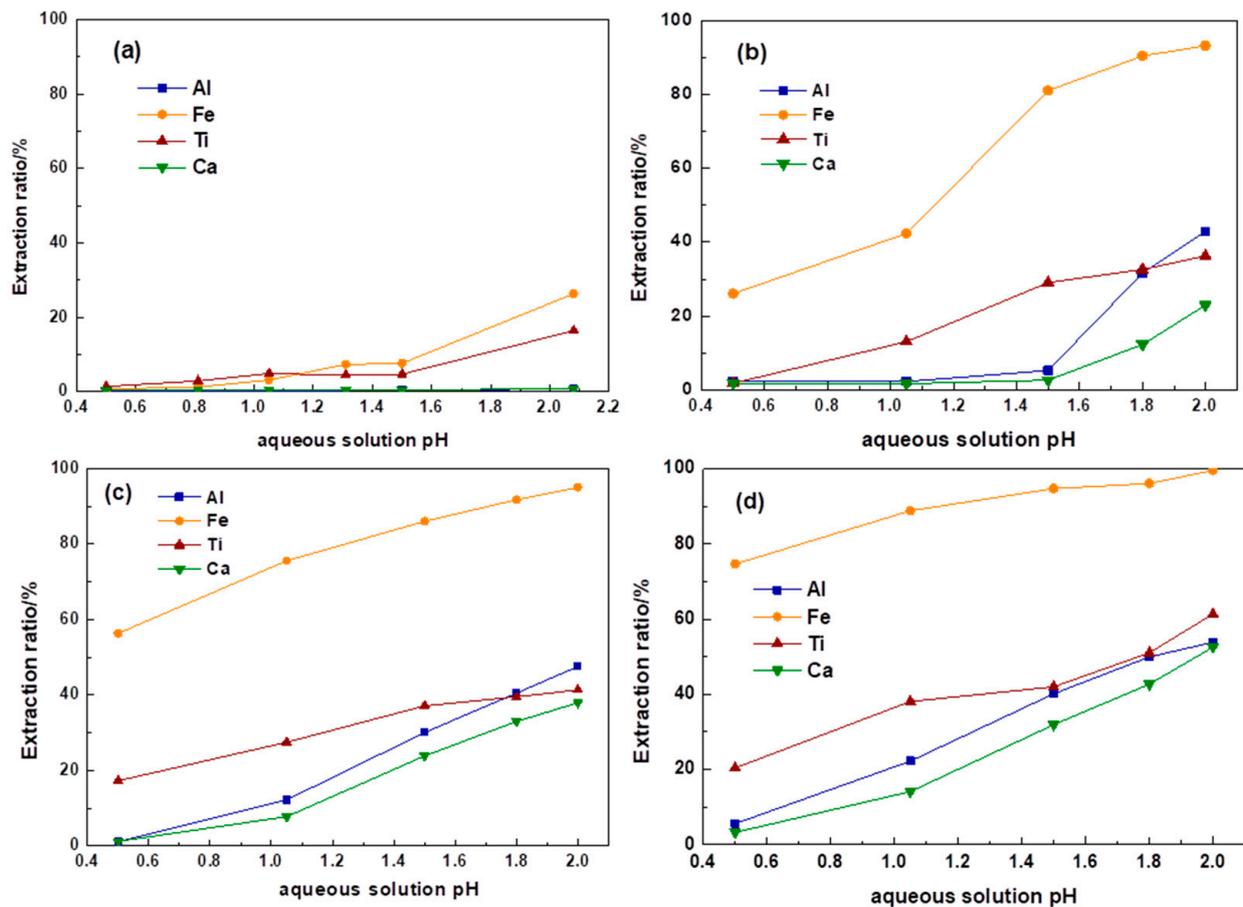


**Figure 4.** Separation coefficients between Sc/Y and La/Ce at P204 concentration of 2% and an initial aqueous solution pH of 1.5.

### 3.2. Separation of REEs against Impurities in the Phosphoric Acidic Leachate

#### 3.2.1. Extraction Behaviors of Impurities in the Phosphoric Acidic Leachate

The extraction behaviors of the dominant impurities of Fe, Al, Ti, and Ca in the phosphoric acidic leachate at different concentrations of P204 and initial aqueous solution pH values are presented in Figure 5. It can be seen in Figure 5a that extremely limited Al and Ca were extracted with P204 at a low concentration of 2% over the whole experimental range of the solution pH values. The extraction ratios of Fe and Ti were less than 5% with the solution pH lower than 1.5 and gradually increased to 26% and 16%, respectively, as the solution pH increased to 2.0.

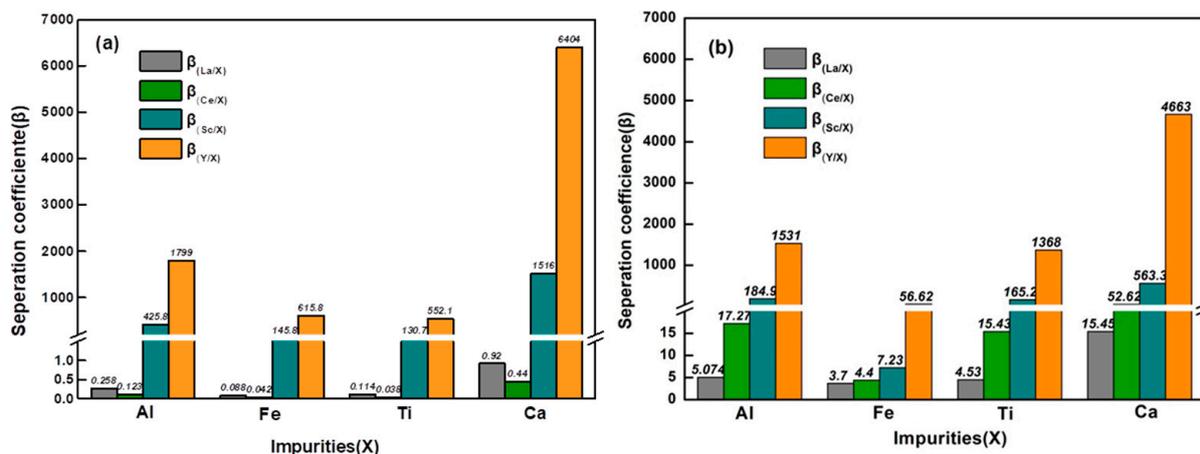


**Figure 5.** Extraction behaviors of impurities at various concentrations of P204 and aqueous solution pH values: (a) 2% P204; (b) 10% P204; (c) 15% P204; (d) 20% P204.

Increasing the concentration of P204 and the solution pH values facilitated the extraction of impurities. The results are shown in Figure 5b–d. When the concentration of P204 was 20%, the extraction ratios of Al and Ca were less than 5%, while those of Fe and Ti attained 74.7% and 20.4%, respectively, at solution pH of 0.5. When the initial solution pH value increased to 2.0, the extraction ratios of Fe, Al, Ti, and Ca attained about 98%, 61.4%, 53.2% and 52.5%, respectively.

### 3.2.2. Separation Coefficients of REEs against Impurities

The separation coefficients of REEs against impurities at P204 concentrations of 2% and 20% when the initial solution pH was 1.5 are presented in Figure 6. High separation coefficients for Sc and Y against the impurities were observed when the P204 concentration was 2%, as shown in Figure 6a. The separation coefficients of Sc against the impurities of Fe, Al, Ti, and Ca were well above 100, while that of Y against the impurities attained a value higher than 500. The  $\beta_{(Y/Ca)}$  was even as high as 6404. Low separation coefficients of La/Ce over impurities were observed as their values were all less than 1 and in the range of 0.1–0.4. This result indicates that the separation of La or Ce against the impurities was poor in this case.



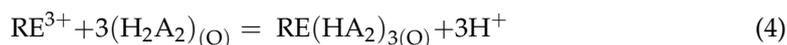
**Figure 6.** Separation coefficients between REEs and impurities with different concentrations of P2O4 at an initial aqueous solution pH of 1.5: (a) 2% P2O4; (b) 20% P2O4.

According to the results obtained, higher concentration of P2O4 of about 20% enhanced the separation of La and Ce against the impurities. The results are shown in Figure 6b. Although the separation coefficients observed for La and Ce against the impurities were not as high as those for Sc and Y, their values were far higher than 1 and were significantly improved to 3–50. The results demonstrate that the separation of La and Ce against the impurities could be realized under this condition.

### 3.3. Mechanism of REEs Extraction from Phosphoric Acidic Leachate with P2O4

#### 3.3.1. Probable Reactions in the Solvent Extraction Processes

The extraction of REEs ions with P2O4 was always regarded as involving a typical ion exchange reaction since the REEs were assumed to exist in the form of simple metal ions in solution. The reaction can be described according to Equation (4). P2O4 generally exists as a dimer in kerosene, and its chemical formula is expressed as H<sub>2</sub>A<sub>2</sub>.



The reaction equilibrium constant K can be calculated according to Equation (5), and the distribution ratio (D) of the rare earth ions (RE<sup>3+</sup>) can be calculated according to Equation (6) after reaction equilibrium.

$$K = \frac{[RE(HA_2)_{3(O)}] \cdot [H^+]^3}{[(H_2A_2)_{(O)}]^3 \cdot [RE^{3+}]} \tag{5}$$

$$D = \frac{[RE(HA_2)_{3(O)}]}{[RE^{3+}]} \tag{6}$$

The extraction equilibrium constant K can be transformed according to Equation (7) based on Equation (6).

$$K = D \cdot \frac{[H^+]^3}{[(H_2A_2)_{(O)}]^3} \tag{7}$$

Applying the logarithm of base 10 (lg) to both sides of Equation (7), Equation (8) is obtained.

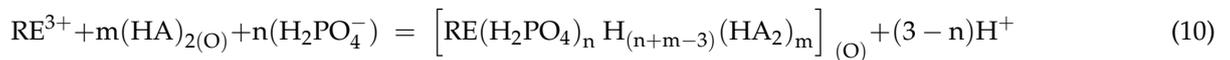
$$\lg D = \lg K + 3\lg[H_2A_2] + 3pH \tag{8}$$

Equation (8) implies that a linear relationship would exist between the lgD of the REEs and the solution pH and the logarithm of the concentration of P204 ( $\lg[H_2A_2]$ ) if the REEs are extracted by P204 through an ion exchange reaction. Both of the slopes for the fitting curve had a value of 3.

However, it was found that P204 would not be ionized, instead being in the form of neutral molecules, when the acidity of the solution was relatively high. The phosphoryl  $P=O$  coordination in the molecular structure of P204 would connect with the rare earth ions during the solvent extraction process—in consequence, a solvation process occurs [36]. This reaction can be described according to Equation (9) in a phosphoric acidic medium since  $H_2PO_4^-$  is the dominant species. In this situation, when the lgD of the REEs was plotted against the solution pH, the slope of the curve was equal to 0.



In the actual extraction process, both an ion exchange reaction and a solvation process could occur. The reaction can be represented by Equation (10). The equilibrium constant  $K$  was calculated according to Equation (11) and further transferred into Equation (12). The slope for the lgD of REEs plotted against the solution pH was between 0 and 3.

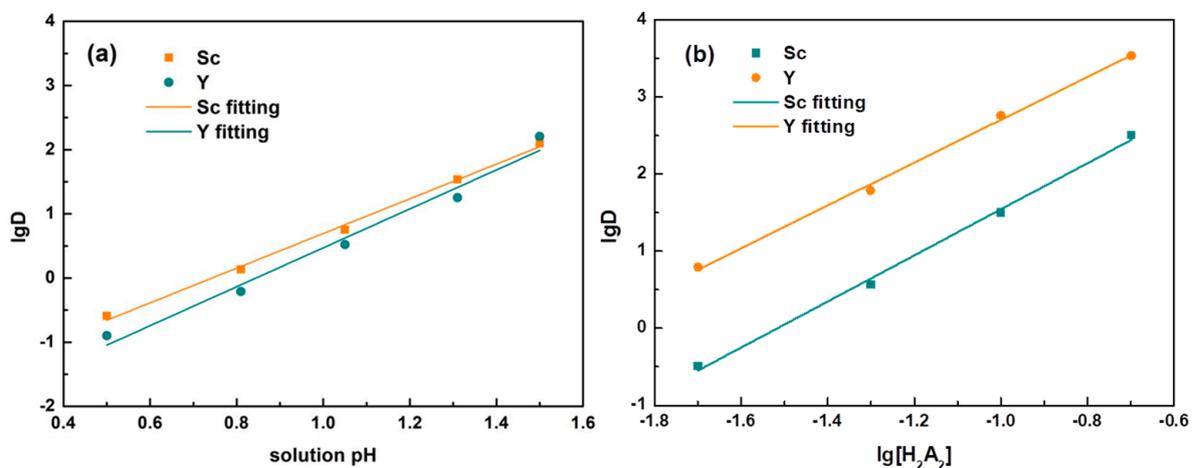


$$K = \frac{[RE(H_2PO_4)_n H_{(n+m-3)}(HA)_m] \cdot [H^+]^{3-n}}{[(H_2A_2)]^m \cdot RE^{3+} \cdot [H_2PO_4^-]^n} \quad (11)$$

$$\lg D = \lg K + m \lg[H_2A_2] + n \lg[H_2PO_4^-] + (3 - n)pH \quad (12)$$

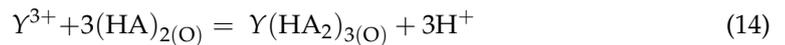
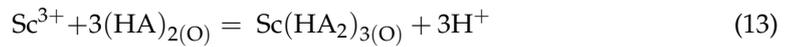
### 3.3.2. Mechanism of Extraction of Sc and Y from Phosphoric Acidic Leachate

To ascertain the reaction of Sc and Y in the phosphoric acidic leachate with P204, the fitting curves of  $\lg D_{(Sc \text{ or } Y)}$  against the solution pH at a P204 concentration of 2%, as well as  $\lg[H_2A_2]$  at a solution pH of 1.5, were plotted, as shown in Figure 7a,b, respectively. It should be noted that the initial aqueous solution pH dropped little after the reaction equilibrium was reached when 2% P204 was used as the extractant. This was because the content of the rare earth elements was extremely low in the acidic leachate and few impurities were extracted with 2% P204.



**Figure 7.** The relationship of lgD against solution pH and  $\lg[H_2A_2]$  for Sc and Y: (a)  $\lg D$ -pH at 2% P204; (b)  $\lg D$ - $\lg[H_2A_2]$  at a solution pH of 1.5.

A linear relationship was obtained when  $\lg D_{(\text{Sc or Y})}$  was plotted against the solution pH after equilibrium; the slopes were, respectively, 2.7 and 3.04, while those for the curve of  $\lg D_{(\text{Sc or Y})}$  against  $\lg[\text{H}_2\text{A}_2]$  were 3 and 2.8, respectively. The fitting equations are shown in Table 4. It was found that all the slopes for the fitting curve for Sc and Y were close to 3, indicating that the extraction of Sc and Y from the phosphoric acidic leachate into the organic phase of P204 was primarily due to an ion exchange process. The reactions can be described according to Equations (13) and (14).

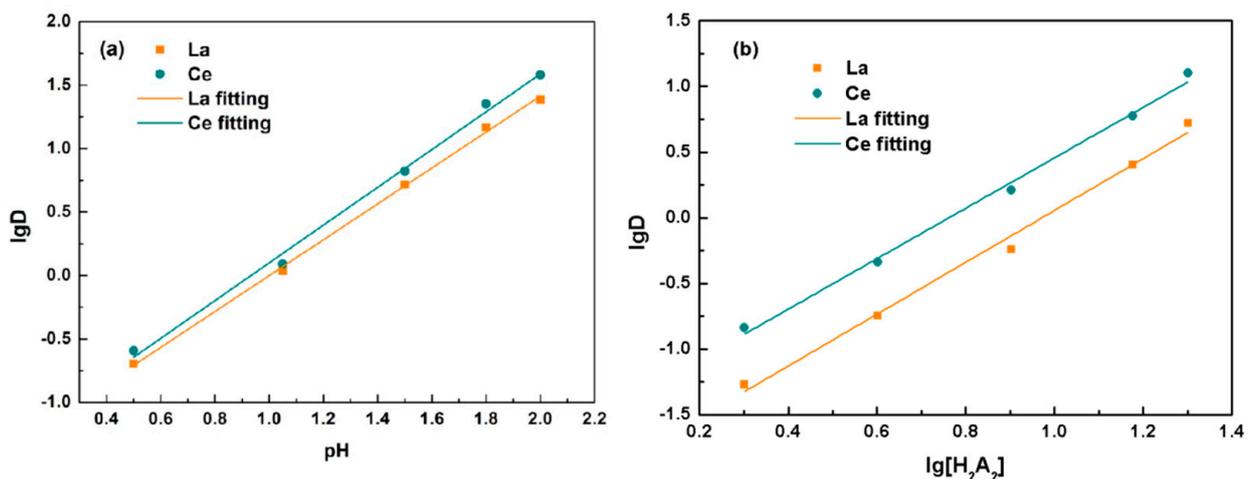


**Table 4.** The fitting equation  $\lg D$ -pH and  $\lg D$ - $\lg[\text{H}_2\text{A}_2]$  for Sc and Y.

Element	$\lg D$ -pH	$R^2$	$\lg D$ - $\lg[\text{H}_2\text{A}_2]$	$R^2$
Sc	$\lg D = 2.70\text{pH} - 2.0$	0.99	$\lg D = 3\lg[\text{H}_2\text{A}_2] + 4.5$	0.99
Y	$\lg D = 3.04\text{pH} - 2.6$	0.97	$\lg D = 2.8\lg[\text{H}_2\text{A}_2] + 5.5$	0.99

### 3.3.3. Mechanism of Extraction of La and Ce from Phosphoric Acidic Leachate

The experimental results indicate that the extraction behaviors of La and Ce were distinct from those of Sc and Y, with a higher concentration of P204 of 20% required for the effective extraction of La and Ce from the phosphoric acidic leachate. Therefore, the extraction mechanism for La and Ce is assumed to be different from that of Sc and Y. It is noteworthy that a drop in the initial solution pH was observed after the reaction equilibrium was reached with 20% P204 as the extractant. The equilibrium pH values of the solution at different initial solution pH values are shown in Figure 8a and the fitting curve of  $\lg D_{(\text{La or Ce})}$  against the equilibrium pH of the solution is also presented. The relationship between  $\lg D_{(\text{La or Ce})}$  and  $\lg[\text{H}_2\text{A}_2]$  is depicted in Figure 8b.



**Figure 8.** The relationship of (a)  $\lg D$ -pH and (b)  $\lg D$ - $\lg[\text{H}_2\text{A}_2]$  for La and Ce.

A clear linear relationship was also observed when  $\lg D_{(\text{La or Ce})}$  was plotted against the equilibrium solution pH and  $\lg[\text{H}_2\text{A}_2]$ . The slopes of  $\lg D$ -pH for La and Ce were 1.7 and 1.8, respectively, while those for  $\lg D$ - $\lg[\text{H}_2\text{A}_2]$  for La and Ce were both calculated as 2. Their fitting equations are shown in Table 5. The slopes were neither 0 nor 3, but located in the range 0–3, indicating that the extraction of La or Ce by P204 was neither a simple ion

exchange reaction nor a solvation reaction, but involved an antagonistic process in which both occurred. The reactions are described according to Equations (15) and (16).



**Table 5.** The fitting equation  $\lg D$ -pH and  $\lg D$ - $\lg[\text{H}_2\text{A}_2]$  for La and Ce.

Rare Earth	$\lg D$ -pH	$R^2$	$\lg D$ - $\lg[\text{H}_2\text{A}_2]$	$R^2$
La	$\lg D = 1.7\text{pH} - 1.4$	0.99	$\lg D = 2.0\lg[\text{H}_2\text{A}_2] + 2.0$	0.99
Ce	$\lg D = 1.8\text{pH} - 1.4$	0.99	$\lg D = 2.0\lg[\text{H}_2\text{A}_2] + 2.3$	0.98

### 3.4. Flowchart of the Extraction of REEs and the Comprehensive Utilization of the Valuable Components in Bauxite Residues

Based on the above results, a stepwise extraction process was proposed and conducted to extract Sc/Y and La/Ce sequentially from the phosphoric acidic leachate of bauxite residues, and an NaOH solution at a concentration of 2 mol/L was further used to extract Sc/Y and La/Ce from the organic phase through a back-stripping process. The organic-to-aqueous ratio was fixed at 1:3 and the duration was 15min at ambient temperature. The REEs contained in the organic phase were effectively extracted and transformed into rare earth hydroxides with extraction ratios higher than 98%. Furthermore, it should be noted that a multistage extraction process would be conducted in the future to eliminate the contamination of impurities for La and Ce resulting from a single extraction process to obtain a pure product of La and Ce.

The proposed extraction/back-stripping process for REEs extraction can be combined with a procedure used in our previous work [32–34] for the stepwise extraction of iron, silica, and alumina titanium with suitable acidic pre-treatment of the bauxite residue. The whole flowchart is presented in Figure 9. Comprehensive extraction of the dominant valuable components in the bauxite residues is enabled through the process shown in the flowchart. In the future, this routine is anticipated to be scaled up and industrialized as the bauxite residue is fully utilized and zero solid waste is produced. As a result, the storage of bauxite residues will be greatly reduced and the pollution stress arising from it on the surrounding environment can be further eliminated.

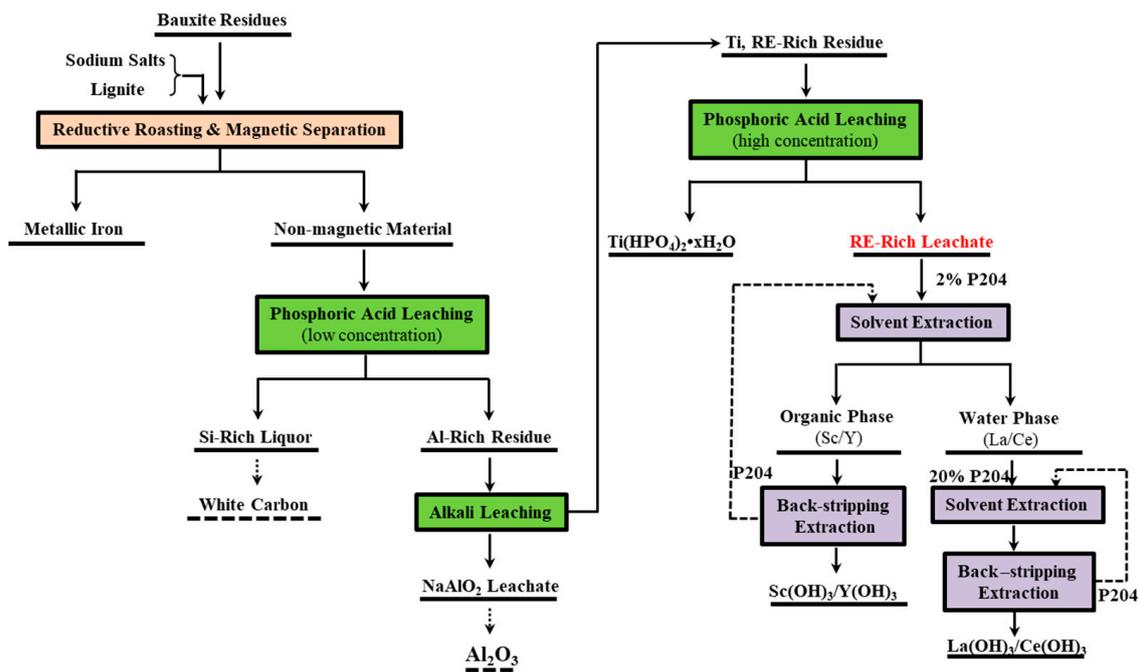


Figure 9. Flowchart of comprehensive utilization of bauxite residues.

#### 4. Conclusions

The distinct extraction behaviors of the REEs La, Ce, Sc and Y and their sequential extraction from the phosphoric acidic leachate of bauxite residues with P204 as an extractant was investigated in this study. The conclusions are as follows:

(1) The REEs of La, Ce, Sc and Y exhibited different behaviors at various concentrations of P204 and initial solution pH values. More than 90% Sc and 98% Y were extracted with P204 at a low concentration of 2% when the solution pH was above 1.5, while less than 5% La and Ce was co-extracted. The extraction ratios of La and Ce attained 87% and 95%, respectively, as the concentration of P204 was increased to 20% at a solution pH of 1.5.

(2) Impurities of Fe, Al, Ti, and Ca in the phosphoric acidic leachate were gradually extracted with increase in the solution pH and concentration of P204, but good separation of REEs against impurities was demonstrated since the separation coefficients were much higher than 1.

(3) A linear relationship was observed when  $\lg D$  of the REEs was plotted against the solution pH and  $\lg [H_2A_2]$ . The slopes for Sc and Y were approximately equal to 3, while those for La and Ce were in the range 0–3. The results indicate that Sc and Y in the phosphoric acidic leachate were extracted by P204 through an ion exchange reaction, but the extraction of La and Ce was due to an antagonistic process whereby an ion exchange reaction and a solvation reaction occurred simultaneously.

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