Simultaneous Recovery of Rare Earths and Uranium from Wet Process Phosphoric Acid using solvent extraction with D2EHPA

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Abstract

In most cases, wet-process phosphoric acid (WPA) contains trace amount of rare earth elements and uranium, which ultimately enter and accumulate in soil and may cause environmental damages. In order to remove and recover these elements, studies about solvent extraction of heavy rare earth elements (HREEs) and uranium (U) with D2EHPA, selective stripping of HREEs from U, and evaporation precipitation of light rare earth elements (LREEs) were investigated. Extraction efficiency of U from WPA was greatly enhanced, but HREEs extraction were significantly retarded when using the solvent mixture of di- (2-ethylhexyl) phosphoric acid (D2EHPA) and tri-butyl-phosphate (TBP) or tri-octyl-phosphine oxide (TOPO) compared with D2EHPA alone. 89.4 % and 94.2% accumulative two-stage extraction efficiencies of HREEs and U, respectively, were achieved with 1.0 M D2EHPA alone. And more than 98.1% HREEs were selectively stripped from loaded D2EHPA with 6.0 M HCl via three stages. In addition, LREEs were enriched to 1204.3 ug/g in evaporation sludge during the concentration process of phosphoric acid from 30% to 50% P₂O₅, and the filtration performance was greatly improved. Based on the studies, an alternative process was developed to recover and group LREEs, HREEs and U during the phosphoric acid production.

Keywords: phosphoric acid, rare earth elements, uranium, solvent extraction, selective stripping, evaporation enrichment

1. Introduction

The rare earth elements (REEs) are a series of elements with similar physiochemical properties including 15 elements of lanthanides, yttrium and scandium. Applications of REEs have been extended to metallurgy, magnets, ceramics, electronics, chemical, optical, medical, nuclear technologies due to their specific physiochemical properties (Habashi, 2013; Krishnamurthy and Gupta, 2004; Xu, 1995). Much research has focused on exploration of green processes for REEs recovery from REEs-dispersed minerals and secondary resources in order to meet the growing demand of REEs, especially for green

energy applications such as battery alloys, solar panels, and wind turbines (Apergis and Apergis, 2017; Liu and Li, 2015). Phosphate rock is considered as one of the most promising new resources for REEs. In addition, considerable amount of U is found in phosphate. Generally, phosphate rock contains about 0.05% REEs and 0.005-0.02% U on average, and the yearly production of phosphate rock all over the world is about 200 million tons (Hurst and Crouse, 1974; Ragheb, 2010). That means about 100 kt REEs and 10 kt U are involved in phosphoric acid production. Without recovery, about 90% U and about 30% REEs would enter and accumulate into soil via fertilizers, that may lead to potential threaten to the environment and human health (Krea and Khalaf, 2000; Reddy et al., 2009).

At present, consumption of phosphate rocks is dominated by the dihydrate phosphoric acid process, which decomposes phosphate rock with sulfuric acid to produce wet process phosphoric acid (WPA) and phosphogypsum (PG) (Zhang, 2014):

In this process, about 20-30% REEs and more than 95% U transferred into WPA. However, the leaching efficiency of REEs up to 75% was achieved with a specific additive under optimized conditions (Sivaprakash, 1989; Wang et al., 2010). The concentration of these elements in WPA range from 10 to 1000 ug/g depends on the composition of phosphate rocks. It was noted that the proportion of heavy rare earth elements (HREEs) in phosphoric acid is higher than that in leaching solution from bastnasite and monazite (Abreu and Morais, 2010; Al-Thyabat and Zhang, 2015a; Al-Thyabat and Zhang, 2015b). Therefore, from the prospect of resources, it is of great significance to recover the REEs and U from WPA.

Since the 1930s, many processes have been proposed for REEs recovery from WPA including crystallization, precipitation, solvent extraction, and ion exchange methods (Habashi, 1985; Wu, 1983). However, due to the high energy consumption of crystallization (Weterings and Janssen, 1985), the impurities involvement, high reagent consumption and phosphorus loss in precipitation processes (Lokshin et al., 2005; Lokshin et al., 2004; Lokshin et al., 2007; Lokshin et al., 2011), the low efficiency of ion exchange (less than 60%) (Reddy et al., 2009; Reddy et al., 2010), these methods did not achieved their industrial applications. Solvent extraction was considered as the most promising method since it is possible to simultaneously recover REEs and U (Beltrami et al., 2014). Organic phosphorus extractants are widely used for REEs and U extraction from WPA. Bunus et al. (Bunus and Dumitrescu, 1992; Bunus et al., 1994; Bunus, 2000) extracted REEs and U with the mixture of D2EHPA+TBP and D2EHPA+TOPO, and stripped REEs and U into green cake with hydrofluoric acid. Krea et al. (Krea and Khalaf, 2000) demonstrated that solvent mixture of di- (octyl phenyl) phosphoric acid (DOPPA)+TOPO did not show significant synergistic effect on REEs and U extraction from WPA under the optimum conditions. Pilot plant tests conducted by Solvay illustrated that mixture of D2EHPA+TOPO could not efficiently extract REEs under the conditions for U extraction (Rollat, 2016). In all these cases, both REEs and U were enriched in the green cake, but the separation of REEs from U required a complex process including acid decomposition, selective extraction, neutralization precipitation

and further treatments. Furthermore, the extraction process of REEs with solvent mixtures were not deeply understood.

In order to solve these challenges, this study investigated the simultaneous extraction of HREEs and U from WPA with D2EHPA, mixture of D2EHPA+TBP and D2EHPA+TOPO, selective stripping of HREEs from loaded D2EHPA. Behaviors of LREEs during the evaporation process of phosphoric acid from 30% to 54% P_2O_5 was also studied. Finally, an alternative process was proposed to recover and group HREEs, U and LREEs during the phosphoric acid production.

2. Experimental

2.1 Materials and chemicals

The di- (2-ethyl hexyl) phosphoric acid with a purity of 95%, tri-n-butyl-phosphate with a purity of 98% and kerosene were provided by Alfa Aesar. Tri-n-octyl-phosphine oxide with a purity of 90% was supplied by Strem Chemicals. Inc. (the structure formula were shown in Tab.2). All other chemicals used were of analytical reagent grade.

The phosphoric acid (brown acid) is produced by dihydrate process from Florida phosphate rock. Before solvent extraction, phosphoric acid needed to go through the following pretreatments (to obtain green acid):

- Using activated carbon to remove organic matters;
- Filtrating through 2-3 cm of bentonite and filter paper to remove suspended particles and organic matters adsorbed on the activated carbon;

Chemical analysis result of acid solution before and after pretreatment were shown in Tab.1 and the pH value of green acid is 0.65.

Tab.1 Chemical analysis of WPA solution before and after pretreatment

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	% P_2O_5	% MgO	% CaO
Before(ppm) ¹	7.0	9.4	1.3	5.2	1.6	3.1	2.8	0.4	28.0	1.4	0.3
After(ppm) ²	6.7	9.3	1.1	4.7	1.3	0.1	2.0	0.3	26.6	1.1	0.0
Element	Dy	Ho	Er	Tm	Yb	Lu	Y	U	REEs	% Fe_2O_3	% Al_2O_3
Before(ppm) ¹	3.1	0.7	2.7	0.5	3.7	0.7	44.8	102.3	90.5	0.9	0.7
After(ppm) ²	2.2	0.3	1.9	0.4	3.4	0.6	52.8	102.7	87.1	1.0	0.7

¹ WPA sample before pretreatment, ² WPA sample after pretreatment, %Oxides: counted by weight percent.

Tab.2 Structural formula of extractants for REEs and U extraction from WPA

2.2 Apparatus and analysis

Chemical composition of aqueous solution was analyzed by ICP-MS (Perkin Elmer Nexion 350X). Solution samples were diluted (100× or 250×) for major oxides analysis (P_2O_5 , MgO , Fe_2O_3 , Al_2O_3) and 50× for Y and U. ICP standards for both REE and major oxides analyses were prepared from single elements standards purchased from Fischer Scientific (Doral, FL, USA). And the acidity of aqueous was measured by a pH meter

2.3 Experimental runs

Extraction and stripping experiments were conducted in conical flasks with intensive magnet stirring and the aqueous solution was separated from organic phase by the aid of separation funnel. D2EHPA, TBP, and TOPO were diluted in kerosene to prepare organic solution. Extraction of U (IV) and U (VI) were conducted before and after oxidation treatment of WPA with 50% H_2O_2 . The extraction performance was evaluated via the distribution coefficient (D_M) and extraction efficiency (E_M) of metal ions which were defined as following equations:

$$D_M = \frac{([M]_{ini} - [M]_{raf}) \left(\frac{V_A}{V_O} \right)}{[M]_{raf}} \quad (2)$$

$$E_M = \left(1 - \frac{[M]_{raf}}{[M]_{ini}} \right) \times 100\% \quad (3)$$

Where $[M]_{ini}$ and $[M]_{raf}$ represent the concentrations of metal ions in the initial and raffinate aqueous solution, and V_A and V_O are the volumes of initial aqueous and organic solution.

Evaporation of phosphoric acid was conducted in a beaker with mild blade stirring in a water bath at 85-88 °C. Then concentrated phosphoric acid was separated from sludge by vacuum filtration with filter cloth.

3. Results and discussion

3.1 Solvent extraction of REEs and U from WPA with D2EHPA, D2EHPA+TBP/TOPO

It was commonly believed that REEs can be co-extracted in the industrial process of U recovery by D2EHPA+TBP and D2EHPA+TOPO. However, according to Solvay's experience, the widely adopted process for U extraction is insufficient to recover REEs (Rollat, 2016). But rare detailed data are available. Therefore, synergistic extraction of

REEs and U from WPA with mixtures of D2EHPA+TBP and D2EHPA+TOPO were investigated.

As clearly demonstrated in Fig. 1 and Fig. 2, a growing synergistic effect for U extraction from WPA was achieved with increasing concentrations of TBP and TOPO in D2EHPA. Especially, a significant enhancement of U extraction was obtained with the mixture of D2EHPA+TOPO. However, extraction efficiencies of HREEs decreased with increasing concentrations of TBP and TOPO, and the detrimental effect was more severe in the case of TOPO. In addition, extraction efficiencies of LREEs are all close to zero with these two kinds of mixture solvents. Furthermore, the loss of phosphorus in these extraction processes are 0.09%, 0.70%, 2.17% P_2O_5 for 1.0 M D2EHPA, 1.0 M D2EHPA+0.1 M TBP, 1.0 M D2EHPA+0.1 M TOPO, respectively.

In conclusion, mixture solvents significantly decreased the extraction efficiencies of HREEs and increased the loss of phosphorus. But, known from Fig.1 and Fig. 2 that D2EHPA was possible to achieve simultaneous recovery of REEs and U. While data about simultaneous recovery of HREEs and U from industrial WPA with D2EHPA alone was rare reported, then studies on the effect of solvent concentration, mixing time, and organic-to-aqueous ratio on extraction efficiency of HREEs and U are needed to obtain the optimal conditions.

Fig. 1. Extraction efficiencies of REEs and U from WPA with mixture of 1.0M D2EHPA and TBP (O/A=1:1, mixing time: 15 min, 23 °C, D2EHPA only: 1.0M D2EHPA without TBP addition)

Fig. 2. Extraction efficiencies of REEs and U from WPA with mixture of 1.0 M D2EHPA and TOPO (O/A=1:1, mixing time: 15 min, 23 °C, D2EHPA only: 1.0 M D2EHPA without TOPO addition)

3.2 Solvent extraction of HREEs and U from WPA with D2EHPA alone

3.2.1 Effect of mixing time on extraction of HREEs and U from WPA with D2EHPA

The equilibrium time can be determined via the extraction kinetics curves. As shown in Fig. 3 and Fig. 4 ten minutes is sufficient for HREEs extraction from WPA. However, in order to guarantee the equilibrium of HREEs extraction was reached, the mixing time was set as fifteen minutes.

Fig. 3. Extraction kinetics of HREEs from WPA with 1.5 M D2EHPA (O/A=1:1, 23 °C)

Fig. 4. Extraction kinetics of U (VI) and U (IV) from WPA with 1.5 M D2EHPA (O/A=1:1, 23 °C)

3.2.2 Effect of O/A ratio on the extraction efficiency of HREEs and U

As is shown in Fig. 5 and Fig. 6, the extraction efficiencies of HREEs and U increase with increasing value of O/A ratio. This could be attributed to the binding between HREEs and U with extra D2EHPA that was brought into the extraction system via elevated organic to aqueous ratio. However, considering the large volume of WPA flow, O/A ratio should be reduced on the premise of effective extraction of HREEs and U. Therefore, O/A=1:1 will be used in subsequent studies.

Fig. 5. Effect of organic/aqueous ratio on HREEs recovery from WPA solution (1.5 M D2EHPA, O/A=1:1, mixing time: 15 min, 23 °C)

Fig. 6. Effect of organic/aqueous ratio on U recovery from WPA solution (1.5 M D2EHPA, O/A=1:1, mixing time: 15 min, 23 °C)

3.2.3 Effect of D2EHPA concentration on the extraction of HREEs and U from WPA

The solvent extraction of REEs and U with D2EHPA from WPA is an ion exchange process between hydrogen ion and metal ions, which takes place at the interface between organic and aqueous phases (Geist et al., 1999). The extraction reaction can be described by equation below (Krea and Khalaf, 2000; Wang et al., 2011):

Where M represents metal ions such as REEs and U, $\overline{HL}$ represents D2EHPA, $\overline{ML_m(HL)_{n-m}}$ represents the coordination compounds. The equilibrium constant of equation (4) was written as K_{ex} :

$$K_{ex} = \frac{[\overline{M(L \cdot HL)_n}][H^+]^m}{[M^{n+}][\overline{HL}]^n} \quad (5)$$

When O/A=1:1, the extraction efficiency of metal ions (E_M) can be defined as:

$$E_M = \frac{[\overline{M(L \cdot HL)_n}]}{[M^{n+}] + [\overline{M(L \cdot HL)_n}]} \times 100\% \quad (6)$$

Combine equation (5) and equation (6) results in the following equation:

$$E_M = \frac{1}{K_{ex} \frac{[H^+]^m}{[\overline{HL}]^n} + 1} \times 100\% \quad (7)$$

In equation (7), K_{ex} is a constant under certain temperature. Hence, extraction efficiency of metal ion increases with increasing concentration of D2EHPA, which was shown as the extraction efficiency curves of HREEs and U in Fig. 7 and Fig.8. However, an elevated concentration of D2EHPA in kerosene leads to the increasing viscosity of organic phase which retards the diffusion of proton and metal ions and results in difficulty of phase separation. Furthermore, stripping of metal ions become more difficult from a metal ion-loaded organic phase with concentrated D2EHPA in kerosene. In addition, it should be noted that extraction efficiencies of LREEs are all close to zero.

Fig. 7. Effect of D2EHPA concentration on HREEs recovery from WPA solution
(O/A=1:1, mixing time: 15 min, 23 °C)

Fig. 8. Effect of D2EHPA concentration on extraction efficiency of U (VI) and U (IV) from WPA
(U(VI) was obtained by oxidation treatment with 50% H_2O_2 0.01 mL/mL WPA, O/A=1:1, mixing time: 15min, 23 °C)

It was noted that U presented in the form of U (IV) in WPA after pretreatment, and that D2EHPA is insufficient for U (IV) extraction since the extraction efficiency of U ranges from 10- 40%. Fortunately, with 0.01 mL hydrogen peroxide (H₂O₂)/mL in WPA, significant enhancement on extraction efficiency of U was achieved due to the oxidation of U (IV) to U (VI). In oxidized form, the binding between U and D2EHPA become more stable in term of the decreased steric hindrance caused by the smaller radius of U (VI).

In conclusion, REEs and U were simultaneously and effectively extracted from WPA by D2EHPA alone. And the optimal conditions for HREEs and U (VI) extraction from WPA with D2EHPA were determined as following: 1.0 M D2EHPA, O/A=1:1, mixing for 15 min at 23 °C. Under the optimal conditions the two-stage accumulated extraction efficiencies of HREEs and U (VI) are 89.4% and 94.2%, respectively.

3.2.4 Mechanism of solvent extraction of REEs and U from WPA with D2EHPA

According to equation (2), with a O/A=1:1, the distribution coefficient is equal to the ratio of metal ionic concentrations in organic to aqueous phase:

$$D_M = \frac{[\overline{M(L \cdot HL)_n}]}{[M^{n+}]} = K_{ex} \frac{[(\overline{HL})_2]^n}{[H^+]^m} \quad (10)$$

Conducting the equation (10) with logarithm transition, the equation can be expressed as:

$$\log D_M = \log K_{ex} + n \log [\overline{HL}] - m \log [H^+] \quad (11)$$

According to equation (11) the value of $\log D_M / \log [\overline{HL}]$ is equal to n that represents the stoichiometric number of D2EHPA. As shown in Fig. 9, the slopes of curves for Y, Tb, and Dy representing heavy rare earth elements (HREEs) are all close to 2.0. That demonstrates that extraction of each HREE requires two D2EHPA molecules. Besides for the low level metal loading conditions, relatively high concentration of D2EHPA presents as dimer in the process of extraction.

On the other hand, in phosphoric acid solution, the dissociation process of H₃PO₄ can be expressed by the following equations:

The acid ionization constant pK for these three equations were defined as pK₁ for equation (12), pK₂ for equation (13), pK₃ for equation (14), respectively. The value of the ionization constants are pK₁=2.14, pK₂=7.20, pK₃=12.34 (Powell et al., 2005) and the pH value of WPA is about 0.65. Which demonstrated that phosphorus was mainly presented in form of H₃PO₄⁰ and H₂PO₄⁻ in 4-6 M H₃PO₄ (for dihydrate process). Hence the reaction equation of HREEs extraction from WPA with D2EHPA can be written as:

As demonstrated in Fig.10, the slope for U (IV) extraction curve is close to 1.0, based on the possible complexes with $(\text{H}_2\text{PO}_4)^-$, the extraction equation was deduced as:

According to the studies by Bunus et al. (Bunus and Dumitrescu, 1986) and Beltrami et al. (Beltrami et al., 2014), U (VI) generally formed $\text{UO}_2(\text{L}\cdot\text{HL})_2$ with D2EHPA, and the slope of $\log D_M / \log[(\text{HL})]$ of U(VI) was close to 2.0 (Fig. 11). Therefore, extraction mechanism of U (VI) with D2EHPA was cation exchange, and complex ion of U (VI) was of +2 valence, the most possible form was $\text{UO}_2(\text{H}_3\text{PO}_4)_2^{2+}$. Thus, the solvent extraction equation of U (VI) from WPA with D2EHPA can be written as:

The complex compounds binding between $\text{REE}(\text{H}_2\text{PO}_4)^{2+}$, $\text{U}(\text{H}_2\text{PO}_4)_3^+$ and $\text{UO}_2(\text{H}_3\text{PO}_4)_2^{2+}$ with D2EHPA can be drawn as the following structure (Tab. 3):

Fig.9 Log D of HREEs vs. log[D2EHPA] at a phase ratio of 1/1

Fig.10 Log D of U (IV) vs. log[D2EHPA] at a phase ratio of 1/1

Fig.11 Log D of U (VI) vs. log[D2EHPA] at a phase ratio of 1/1

Tab.3 Molecule structures of complexes between metal ions and D2EHPA

3.2.7 Selective stripping of HREEs from loaded organic phase

High concentration HCl (6 M) was used for selective stripping of HREEs from loaded D2EHPA owing to its wide industrial application. Stripping experiments demonstrated that 98.1% of accumulated stripping efficiency was achieved via three stages, and the loss of U during the process was less than 1%. Moreover, it was found that the HREEs can be accumulated in HCl solution via circulating the aqueous solution (Fig. 12). The maximum concentration of HREEs in HCl solution was determined by the distribution coefficients of HREEs between organic and aqueous phases as well as the initial concentration of HREEs in loaded organic phase. For uranium, 97.8% of stripping rate was achieved with 15% HF or 20% Na_2CO_3 .

Fig. 12. Selective stripping of HREEs from loaded D2EHPA with 6 M HCl (6 recycles)
(O/A=1:1, 23 °C, HREEs in loaded D2EHPA is 58.8 ppm)

3.3 Precipitation of LREEs from WPA via evaporation

Known from previous studies, D2EHPA is insufficient for LREEs extraction from WPA (Bunus et al., 1994). Our results also shown that LREEs were completely left in raffinate after two stages of solvent extraction of HREEs and U with D2EHPA. Fortunately, solubility of REEs in phosphoric acid shows a dramatic difference from that of REEPO₄ in non-phosphate solution. LREEs have far lower solubility in WPA than HREEs, for example, solubility of Y₂O₃ in WPA is about 48.8 g/L while solubility of La₂O₃ is about 0.18 g/L (Lokshin et al., 2007). Therefore, evaporation method-a general process for the commercial grade phosphoric acid production was adopted for LREEs enrichment from WPA. The chemical analysis of evaporation sludge is given in Tab.4, and the composition of concentrated phosphoric acid is displayed in Tab.5. The results demonstrate that more than 90% of TLREEs were precipitated and enriched in evaporation sludge with a concentration of 1204.3 ug/g LREEs. Furthermore, 77.4% precipitation ratio was also achieved for Gd which has a relatively low extraction efficiency with D2EHPA from WPA.

Tab.4 Composition of evaporation sludge (ICP-MS)

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	% P ₂ O ₅	% MgO	% Na
Con./ppm	351.9	481.6	56.4	257.9	48.2	8.3	47.6	3.4	30.1	0.8	0.6
Element	Dy	Ho	Er	Tm	Yb	Lu	Y	U	% Al ₂ O ₃	% Fe ₂ O ₃	% K

Con./ppm	6.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.6	0.7	0.1
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Tab.5 Concentration of ions in concentrated phosphoric acid (54% P₂O₅)

Element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	% P ₂ O ₅	% MgO	% Na
Lab(ppm)	0.4	0.6	0.1	0.5	0.5	0.2	1.9	0.3	55.9	1.4	0.0
Plant(ppm)	0.6	0.6	0.1	0.3	0.2	0.1	0.9	0.3	56.0	1.1	ND
Element	Dy	Ho	Er	Tm	Yb	Lu	Y	U	% Al ₂ O ₃	% Fe ₂ O ₃	% K
Lab(ppm)	1.3	0.1	0.1	0.0	0.0	0.0	2.6	2.0	2.3	1.5	0.0
Plant(ppm)	2.9	0.9	4.5	0.9	7.1	1.5	75.9	235.0	1.0	1.7	ND

a: concentrated phosphoric acid obtained by lab-scale experiment. b: concentrated phosphoric acid produced by plant. %Oxides: counted by weight percent. ND: not determined.

Moreover, a significant improvement on filtration speed of concentrated phosphoric acid (54% P₂O₅) was achieved in the case of evaporation process of green acid. In practice, in order to extract HREEs and U from WPA at the same time, the WPA solution was required to go through an uranium (U (IV)) oxidation treatment to obtain the brown acid. While the brown acid is difficult to filter afterward. It is also a major issue in commercial grade phosphoric acid production. Oxidation process of WPA with 50% H₂O₂ was investigated to achieve a good filtration performance concentrated phosphoric acid. It was noted that the oxidized brown WPA solution turned green gradually during the long time standing (Table. 6). Which demonstrates that the Fe²⁺ ions were oxidized to Fe³⁺ at beginning and then reduced back to Fe²⁺. This mechanism was illustrated by Singh et al. (Singh et al., 2001) that redox potential of WPA was elevated by addition of 50% H₂O₂ until reaching the maximum value in a short period of time and then decreased gradually and the maximum redox potential was determined by the dosage of H₂O₂. Therefore, treated WPA with 50% H₂O₂ for the extraction of U(VI) and HREEs, and then stood the raffinate for more than 12 h before the evaporation operation to achieve LREEs enrichment and an easy-to-filter concentrated phosphoric acid.

Table.6 Color change of WPA before and after oxidation

Before oxidation	60s after oxidation	3h after oxidation	7h after oxidation	20h after oxidation

Note: the right one is the fresh WPA suffered pretreatment, the left one has gone through one oxidation operation.

3.4 Suggested alternative process for recovery of REEs and U.

Fig. 13 An alternative process for simultaneous recovery and grouping of HREEs, LREEs and U from WPA

Based on the studies above, an alternative process was proposed and recommended for recovery and grouping of HREEs, LREEs and U from WPA (Fig. 13). In this process, WPA was treated with activated carbon and bentonite before filtration, then HREEs and U were extracted from WPA with 1.0 M D2EHPA. 6.0 M HCl solution was used to selectively stripped HREEs from loaded D2EHPA, followed by U stripping by 5- 15% HF or 10- 20% Na₂CO₃ solutions. LREEs that were left in raffinate would be enriched by heating WPA up to 85-88 °C and insulated for several hours until the phosphoric acid was concentrated to 54% P₂O₅. In this process, more than 90% of REEs and U were removed and recovered from phosphoric acid.

4. Conclusions

Simultaneous extraction of HREEs and U was achieved by 1.0 M D2EHPA alone, the accumulated two-stage extraction efficiencies for HREEs and U are 89.4% and 94.2% under the optimal conditions: O/A=1:1, mixing 15 min, at 23°C. 98.1% HREEs were selectively stripped by 6.0 M HCl via three stages and 97.8% U was then precipitated by 15% HF or 20% Na₂CO₃. LREEs were enriched during the evaporation process in a easy-soluble form and the filtration performance of concentrated phosphoric acid was significantly improved. Based on the studies above, a alternative process is developed to recover REEs and U from WPA, that avoids the complex process of REEs separation from green cake. And the preliminary experimental results showed that more than 90% of REEs and U were recovered.

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