Thermodynamic study of W(VI) extraction using amine-based extractant and phosphonium ionic liquids

Tatsuki Igosawa[1], Yusuke Tsuchida[1], Masahiko Matsumiya[1*] and Yuji Sasaki[2]

[1] Graduate School of Environment and Information Sciences, Yokohama National University,
79-2 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
[2] Nuclear Science and Engineering Directorate, Japan Atomic Energy Agency,
Tokai-mura, Naka-gun, Ibaraki, 319-1195, Japan
[*]E-mail: matsumiya-masahiko-dh@ynu.ac.jp, Tel: +81-45-339-3464, FAX: +81-45-336-4332

Abstract

The triethyl-n-pentyl phosphonium bis(trifluoromethylaulfonyl)amide ionic liquid (IL) and Alamine 336 was employed as the diluent and the extractant for the selective separation of W(VI) by solvent extraction (SX), respectively. The extraction mechanism of W(VI) was based on the ion association reaction; $[H_xW_yO_z^{n-}]_{aq}$ + $n[R_3NH^+Cl^-]_{IL}$ + $\rightleftarrows$ $[(R_3NH)_nH_xW_yO_z]_{IL}$ + $[Cl^-]_{aq}$, where x, y, z, and n are the stochiometric coefficients related to the complexation state and are dependent on the pH. Arrhenius plot of the operating temperatures at 298-368 K yielded the linear relation. Thermodynamic result indicated the positive enthalpy for W(VI) and favored the endothermic nature of the extraction reaction.

Moreover, the repeated use of $[R_3N]/[P_{2225}][NTf_2]$ medium was researched by continuous SX and stripping process using 3.0 mol dm^{-3} HCl, NH$_4$OH and NaOH media. For the five cycles on SX, the extraction percentage of W(VI) at 91.6−98.4% was high value. Then, the optimal stripping medium was found to be 3.0 mol dm^{-3} NH$_4$OH solution. The stripping percentage of W(VI) reached to be 100 % on the condition of 8<pH by the stripping reaction; $[(R_3NH)_n(H_xW_yO_z)]_{IL}$ + $n[NH_4OH]_{aq}$ $\rightleftarrows$ $[(NH_4)_n(H_xW_yO_z)]_{aq}$ + $n[R_3NH^+OH^-]_{IL}$. Finally, the crystallization reaction occurred at pH∼5 and the obtained precipitates were identified as the ammonium paratungstate by XRD. A series of novel hydrometallurgical process using ILs enabled us to conclude that W(VI) component was efficiently recovered from spent tungstophosphate catalyst.

Keywords

Ionic liquids, Solvent extraction, Thermodynamics, Tungsten

1. Introduction

Tungsten is widely applied for high temperature and strength industries. The chemical synthesis process using the solid acid catalyst including tungstophosphate was widely used in recent years. Supported tungsten oxide catalytic materials have been extensively applied for numerous petroleum chemistry such as hydrocarbon cracking [1,2], olefin metathesis [3-5] and catalytic reaction [6-9]. The actual spent catalysts included the tungsten components and a small amount of phosphate in the heteropolyacid $H_3PW_{12}O_{40}$ structure. The heteropolyacid $H_3PW_{12}O_{40}$ was demonstrated by Keggin as an edge shared polyhedral structure [10]. The $H_3PW_{12}O_{40}$ was one of the heteropolyacid and tend to use the acidic medium, which are applied as a catalyst [11,12]. After the use of the solid catalyst for organic reaction, it is important to selectively separate the phosphate in the heteropolyacid in order to reuse the tungsten components. It was reported that $H_3PW_{12}O_{40}$ decomposed to $[PO_4^{3-}]$ and $[WO_4^{2-}]$ with the addition of NaOH through several intermediates [13]. Therefore, it is important to develop the selectively separation technology for the $[PO_4^{3-}]$ component and convert the useful tungsten compounds.

Solvent extraction (SX) is a hopeful separation technique to recover tungsten complex; W(VI) [14,15]. Aliphatic amines have been generally employed in the acidic condition as extractants [16-19]. The concentration (<10 vol.%) of the extractant was desirable to prevent the emulsification [20]. Third petroleum such as kerosene is widely applied as a diluent, however, the presence of phase modifiers is usually necessary, because amino tungstate complexes are insoluble in the organic phase. In the present study, in a departure from the conventional SX approach, we investigated the feasibility of using a phosphonium-based ionic liquid (IL) as the medium for the separation of W(VI). A well-known amine with the molecular formula (tri-octyl/decyl amine, R_3N; R = $CH_3(CH_2)_7$-/$CH_3(CH_2)_9$-), Alamine 336 (A336), was chosen as the preferred extractant, because it offers many advantages such as negligible solubility in the aqueous phase, high boiling point, low density, and easy handling [21]. We have demonstrated that the recovery of W(VI) components from WC-Co hard metal wastes by hydrometallurgy [22]. Appling the hydrometallurgical technique, the objective of this study is to develop a novel hydrometallurgical process to separate $[PO_4^{3-}]$ from spent tungstophosphate catalyst and recover the tungsten compounds. This process involves the following steps: leaching, precipitation separation, SX using ILs and crystallization-stripping as shown in **Fig. 1**.
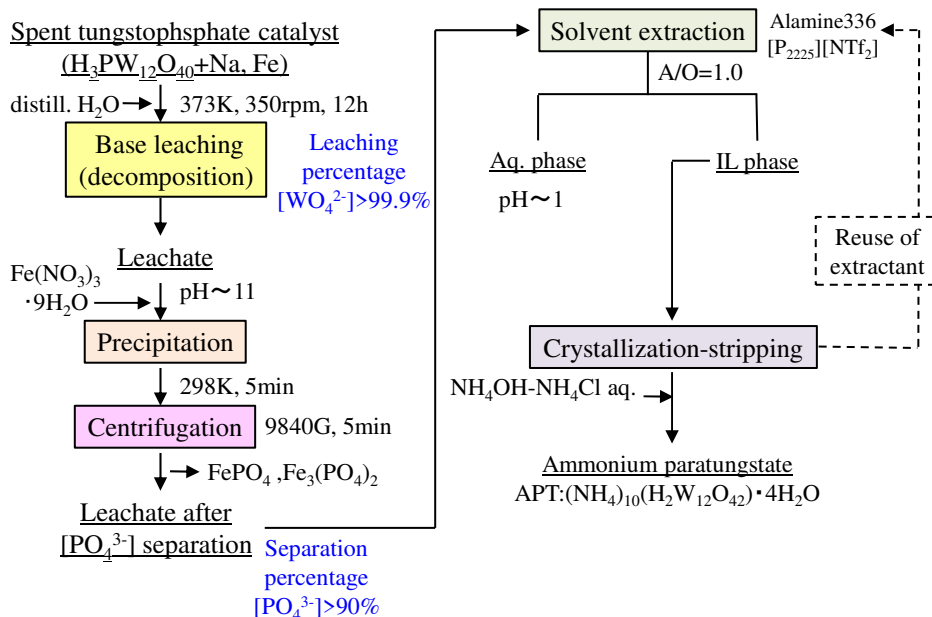
Fig. 1 A novel hydrometallurgical process of spent tungstophosphate catalyst.

2. Experimental

2.1 Sample preparation

The IL triethyl-*n*-pentyl phosphonium bis(trifluoromethyl-sulfonyl)amide ($[P_{2225}][NTf_2]$) was synthesized from the metathesis reaction using $[P_{2225}]Br$ (Nippon Chemical Industrial Co., Ltd., >99.5 %) as a precursor with $Li[NTf_2]$ (Kanto Chemical Co., Inc., 99.7 %) in distilled water at 343 K [23]. The obtained $[P_{2225}][NTf_2]$ in the lower phase was washed with distilled water at several times to remove halogen ions, followed by evaporation at 423 K for 24 h. The obtained $[P_{2225}][NTf_2]$ was then dried under high vacuum (<0 kPa) at 393 K for 48 h.

2.2 Solvent extraction (SX)

The SX process was applied to effectively separate W(VI) component from the solution after the separation of $[PO_4^{3-}]$ component. For the SX process, Alamine336 (tri-octyl/decyl amine, R_3N; R = $CH_3(CH_2)_7$-/$CH_3(CH_2)_9$-, A336) was selected as the extractant for W(VI) because of its high solubility in ILs and high hydrophobicity. A336 is a C8−C10 saturated straight-chain tertiary amine mixture, and the pale yellow extractant is insoluble in water (< 5 mg dm^{-3}). A336 has an average molecular weight of 392 g mol^{-1}, and its density and viscosity at 303 K are 0.81 g cm^{-3} and 11 mPa·s, respectively. The $[P_{2225}][NTf_2]$ was applied as the diluent for SX process. After the leachate was separated the $[PO_4^{3-}]$ component at the separation percentage of 90% by the precipitation reaction, the leachate was prepared on the condition of pH=1.0-4.0 to act as the aqueous phase for SX. The A336 concentration in the IL

phase was 1.0 mol dm^{-3}. The change in pH at equilibrium was precisely measured by a high-precision digital pH meter (MM-43X, DKK-TOA, Corp.). The SX procedure was carried out with an aqueous to IL phase ratio of 3:1 by volume. The solution with two phases was stirred in a sampling bottle at a speed of 350 rpm for 12 h. The operating temperature was changed from 298 K to 368 K. The concentrations of the metal ions in the aqueous phase before and after the equilibrium were measured by ICP-AES (ICP-AES, ICPE-9000, Shimadzu Co.). The concentration of the metal ions in the IL phase after the equilibration was calculated using a mass balance relation. The distribution ratio (D) and extraction efficiency (E) were calculated from the quantitative data by ICP-AES analysis as follows.

$$D=\frac{[M]_{aq}^{ini}-[M]_{aq}^{fin}}{[M]_{aq}^{fin}}, \quad E(\%)=\frac{100D}{D+V_{aq}/V_{IL}} \qquad (1)$$

where [M] and V express the concentration of the metal ions and the volume, respectively. Subscripts 'aq' and 'IL' represent the aqueous and IL phases, respectively. The expressions of 'ini' and 'fin' imply the initial and final concentrations, respectively.

2.3 Continuous SX and stripping process

The SX and the stripping for five cycles were carried out to evaluate the repeated use of [R$_3$N]/[P$_{2225}$][NTf$_2$] medium. For SX, 1.09 mmol dm^{-3} W(VI) was used as the aqueous phase. The volume ratio (A/O) of the aqueous and IL phases was prepared at A/O=1.0. After 1st-SX, 1st-stripping procedure was applied for three kinds of media, which are 3.0 mol dm^{-3} HCl, NH$_4$OH and NaOH aqueous solution. After 1st-stripping, new aqueous phase containing 1.09 mmol dm^{-3} W(VI) was introduced into the IL phase on 2nd-SX. After 2nd-SX, 2nd-stripping was executed with the same conditions. Thus, SX-stripping procedure was repeatedly carried out at five cycles. The metal concentration in the IL phase at each cycle was measured by ICP-AES. The extraction efficiency (E) for SX and stripping was similarly evaluated from the quantitative data.
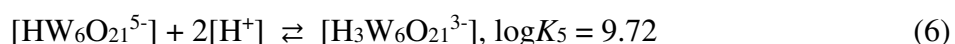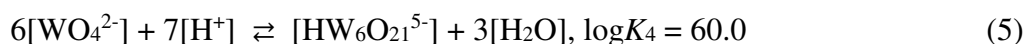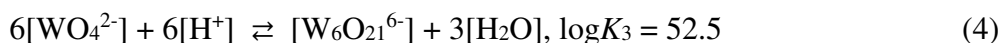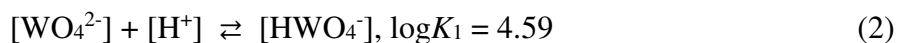
2.4 Crystallization-stripping

After SX process, the crystallization-stripping was carried out to obtain the ammonium paratungstate (APT, (NH$_4$)$_{10}$(H$_2$W$_{12}$O$_{42}$)·4H$_2$O). The 3.0 mol dm^{-3} NH$_4$OH solution including NH$_4$Cl was selected as crystallization agent, because it is reported that the stripping of W(VI) is normally performed with NH$_4$OH-NH$_4$Cl solution and the product is usually recovered as APT [24,25]. The concentrations of the metal ions in the aqueous phase before and after the equilibrium were measured by ICP-AES. The distribution ratio (D) and extraction efficiency (E) for stripping were similarly calculated from the quantitative data. After the

crystallization-stripping operation, the crystalized product was separated by a filtration and dried at 298 K for 24 h. The product obtained by crystallization was identified by X-ray diffraction (XRD, SmartLab, Rigaku Co.)

3. Results and discussion

3.1 Extraction mechanism

It is important to comprehend the distribution behavior of tungstate ions in pH range. The following equilibrium constants [26] were reported in different pH ranges.

$$[WO_4^{2-}] + [H^+] \rightleftarrows [HWO_4^-], \log K_1 = 4.59 \tag{2}$$
$$[WO_4^{2-}] + 2[H^+] \rightleftarrows [H_2WO_4], \log K_2 = 8.10 \tag{3}$$
$$6[WO_4^{2-}] + 6[H^+] \rightleftarrows [W_6O_{21}^{6-}] + 3[H_2O], \log K_3 = 52.5 \tag{4}$$
$$6[WO_4^{2-}] + 7[H^+] \rightleftarrows [HW_6O_{21}^{5-}] + 3[H_2O], \log K_4 = 60.0 \tag{5}$$
$$[HW_6O_{21}^{5-}] + 2[H^+] \rightleftarrows [H_3W_6O_{21}^{3-}], \log K_5 = 9.72 \tag{6}$$

According to the above equilibrium constants, the distribution of tungstate ions was evaluated as a function of pH as shown in **Fig. 2**. This result indicated that the tungstate ions existed as the anionic species in the wide pH range and amine extractant would be effective to selectively extract these tungsten complexes.
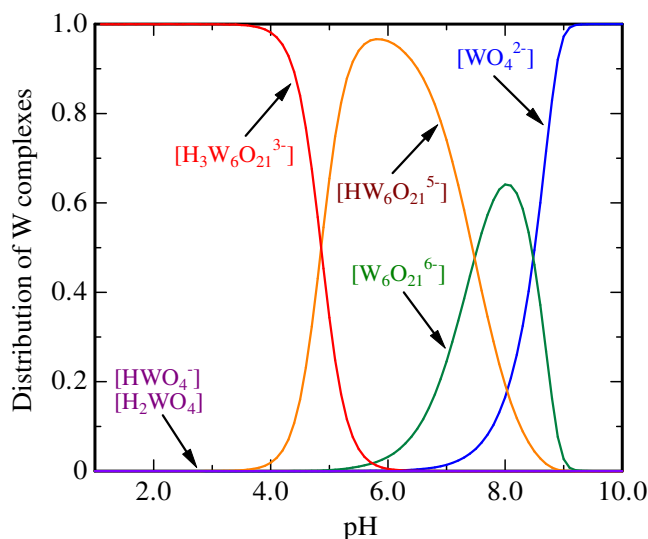
Fig. 2 Relationship between distribution of various tungstate ions and pH in aqueous phase.

In addition, the extraction of W(VI) was dependent on the pH of the aqueous phase. This extraction tendency was consistent with the results using amine-based extractants [27,28]. For the extraction of W(VI), the ion association reaction would be represented as follows:

$$[R_3N]_{IL} + [HCl]_{aq} \rightleftarrows [R_3NH^+Cl^-]_{IL} \tag{7}$$

$$[H_xW_yO_z{}^{n-}]_{aq} + n[R_3NH^+Cl^-]_{IL} \rightleftarrows [(R_3NH)_nH_xW_yO_z]_{IL} + n[Cl^-]_{aq} \tag{8}$$

The extraction equilibrium constant (K_{ex}) and the distribution ratio (D) are expressed the following equations.

$$K_{ex}=\frac{[(R_3NH)_nH_xW_yO_z]_{IL}[Cl^-]_{aq}^n}{[H_xW_yO_z^{n-}]_{aq}[R_3NH^+Cl^-]_{IL}^n}, \quad D=\frac{[(R_3NH)_nH_xW_yO_z]_{IL}}{[H_xW_yO_z^{n-}]_{aq}} \tag{9}$$

The following relationship is obtained from Eq. (9).

$$K_{ex}=\frac{D[Cl^-]_{aq}^n}{[R_3NH^+Cl^-]_{IL}^n} \tag{10}$$

The logarithm of D is expressed as follows, according to the relation in Eq. (10):

$$\log D=\log K_{ex} + n\log[R_3NH^+Cl^-]_{IL}-n\log[Cl^-]_{aq} \tag{11}$$

where x, y, z, and n are the stochiometric coefficients and are dependent on the pH [29]. Considering from the W(VI) complex formation in **Fig. 2**, $[H_xW_yO_z{}^{n-}]$ could be expressed as $[H_3W_6O_{21}{}^{3-}]$ ($x=3$, $y=6$, $z=21$, $n=3$) for pH=1.0-4.5, $[HW_6O_{21}{}^{5-}]$ ($x=1$, $y=6$, $z=21$, $n=5$) for pH=4.5-6.5, $[W_6O_{21}{}^{6-}]$ ($x=0$, $y=6$, $z=21$, $n=6$) for pH=6.5-8.5, and $[WO_4{}^{2-}]$ ($x=0$, $y=1$, $z=4$, $n=2$) for pH=8.5-10.0, respectively. This complexation state also indicated the declining trend of the extraction percentage for W(VI) with the alteration of pH. The separation factor ($\beta_{W/P}$) between W(VI) and P(III) in this $[R_3N]/[P_{2225}][NTf_2]$ system was tabulated in **Table 1**. In the case of pH=1.03, high separation factor; $\beta_{W/P}$ =100.8 was demonstrated and the phosphonium-based IL with high dielectric constant would be useful for the separation of W(VI).

Table 1 Separation factor ($\beta_{W/P}$) for each pH condition by solvent extraction

Condition	$E(W)/\%$	$E(P)/\%$	$\beta_{W/P}$	T/K
pH=1.03	94.6	13.4	100.8	
pH=2.01	81.3	14.3	26.1	
pH=3.04	55.8	12.3	9.0	298.15
pH=4.02	44.3	11.9	5.9	
pH=5.01	26.1	9.8	3.3	

The extraction behavior and the slope analysis of W(VI) for [R_3N]/[P_{2225}][NTf_2], $R=(CH_2)_7CH_3/(CH_2)_9CH_3$ at pH=1.0 were shown in **Fig. 3(a)** and **3(b)**, respectively. The extraction percentage (*E*) of W(VI) was increased with increasing the concentration of the extractant in [R_3N]/[P_{2225}][NTf_2] system. From the plot of log*D* vs. log[A336]$_{IL}$, the respective slope of 2.7 indicated the association of three moles of the extractant with one mole of W(VI) during extraction. Therefore, the extraction of W(VI) at pH=1.0, the ion association reaction was represented as follows:

$$[H_3W_6O_{21}{}^{3-}]_{aq} + 3[R_3NH^+Cl^-]_{IL} \rightleftarrows [(R_3NH)_3H_3W_6O_{21}]_{IL} + 3[Cl^-]_{aq} \tag{12}$$
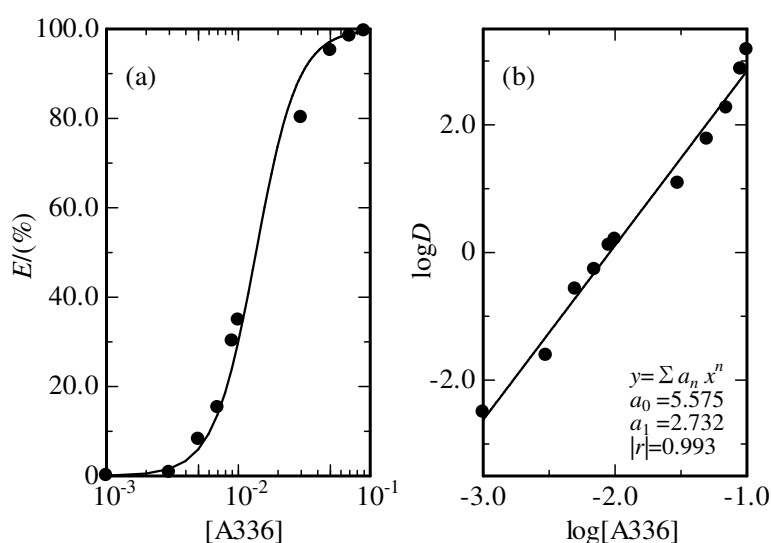
Fig. 3 Extraction behavior of W(VI) using [R_3N]/[P_{2225}][NTf_2] system at pH=1.0.
(a) Extraction percentage of W(VI) and (b) slope analysis

The temperature dependence of the W(VI) extraction was investigated to ascertain the thermodynamic behavior. Thermodynamic results support to predict the complexation state of target species with extractants while separating it from the abundant wastes. Moreover, the distribution coefficient is strongly associated with the operating temperature of the extraction process. The extraction perentage of W(VI) was relatively increased with elevating the operating temperature. The enhancement of the extraction performance indicated the endothermic nature of the extraction reaction. Thermodynamic parameters such enthalpy (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) were evaluated based on the thermodynamics as follows.

$$\Delta G = -RT\ln K_{ex} = \Delta H - T\Delta S \tag{13}$$

The plot of the natural logarithm of K_{ex} versus the inverse of the absolute temperature yields a slope proportional to the enthalpy (ΔH)

$$\log D = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} + \log[Cl^-]_{aq} - \log[R_3NH^+Cl^-]_{IL} \qquad (14)$$

As shown in **Fig. 4**, Arrhenius plot could yield the slope and the intercept, which correspond to the enthalpy and the entropy, respectively. The positive value of resulting enthalpy for W(VI) relatively favors endothermic behavior.
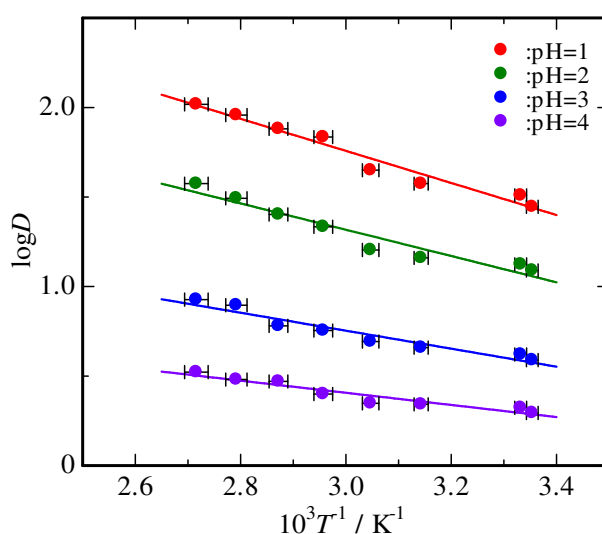
Fig. 4 Arrhenius plot of W(VI) on [R$_3$N]/[P$_{2225}$][NTf$_2$] system.

The evaluated thermodynamic parameters were listed in **Table 2**. The positive value of ΔS implies the extraction reaction proceeds spontaneously in this system. Then, the randomness in this system was favored in pH=1.0, because ΔS value in pH=1.0 was largest in whole pH conditions. Therefore, ΔS value in pH=1.0 directly would be acted on the total negative alternation in Gibbs energy on the extraction reaction. A series of tendency of the thermodynamic parameters for W(VI) extraction was consistent with the Aliquat336 extraction system [30].

Table 2 Thermodynamic parameter of extraction for W(VI) on $[R_3N]/[P_{2225}][NTf_2]$ system.

Condition	ΔH/kJ mol^{-1}	ΔS/J K^{-1}mol^{-1}	ΔG/kJ mol^{-1}	T/K
pH=1.0	17.17	85.15	-8.22	
pH=2.0	14.06	67.40	-6.04	298.15 ± 0.80
pH=3.0	9.62	43.29	-3.28	
pH=4.0	6.50	27.30	-1.64	
pH=7.0 [30] using Aliquat336	11.97	46.70	-1.95	298.15

3.2 Continuous SX and stripping process

The repeated use of $[R_3N]/[P_{2225}][NTf_2]$ medium for consecutive SX-stripping procedure was researched in this study. A series of SX and stripping results at five cycles was listed in **Table 3**. For the 1st-5th cycles of SX process, the high extraction percentage of W(VI) at 91.6-98.4% was demonstrated in this system. On the other hand, 3.0 mol dm^{-3} NH$_4$OH base medium was found to be optimal reagent, although acid medium was unsuccessful due to the stability of W(VI) complex in the acidic region. Then, NH$_4$OH medium was hopeful as a stripping agent, because the ammonium paratungstate (APT) was formed by the crystallization-stripping process. As a result, it was demonstrated that $[R_3N]/[P_{2225}][NTf_2]$ medium could repeatedly be used for continuous SX-stripping process.

Table 3 The result of W(VI) for solvent extraction (SX) and stripping process at five cycles.

No.	SX	Stripping		
	E/%	E/%(HCl)	E/%(NH$_4$OH)	E/%(NaOH)
1st	98.4	18.6	90.6	79.2
2nd	96.1	16.4	87.1	80.4
3rd	94.3	15.1	78.2	78.1
4th	92.1	14.2	76.4	76.3
5th	91.6	10.8	70.1	*71.6*

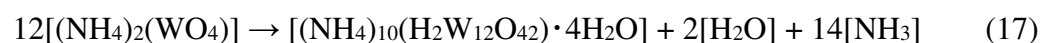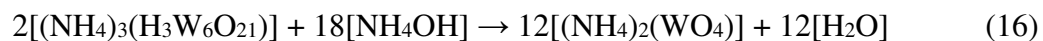## 3.3 Crystallization-stripping of W(VI)

In order to obtain the ammonium paratungstate (APT) the crystallization-stripping was applied for the IL phase after SX. The stripping percentage of W(VI) reached to be 100 % on the condition of 8<pH as shown in **Fig. 5**. The stripping reaction would be based on the following reaction.

$$[(R_3NH)_n(H_xW_yO_z)]_{IL} + n[NH_4OH]_{aq} \rightleftarrows [(NH_4)_n(H_xW_yO_z)]_{aq} + n[R_3NH^+OH^-]_{IL} \quad (15)$$

where x, y, z, and n are the stochiometric coefficients. The complexation states of the stripping

procedure are also dependent on the pH [29]. Then, the complex of W(VI); $[(NH_4)_n(H_xW_yO_z)]$ for stripping would be expressed as $[(NH_4)_3(H_3W_6O_{21})]$ ($x=3$, $y=6$, $z=21$, $n=3$) for pH=1.0-4.5, $[(NH_4)_5(HW_6O_{21})]$ ($x=1$, $y=6$, $z=21$, $n=5$) for pH=4.5-7.0, $[(NH_4)_6(W_6O_{21})]$ ($x=0$, $y=6$, $z=21$, $n=6$) for pH=7.0-8.5, and $[(NH_4)_2(WO_4)]$ ($x=0$, $y=1$, $z=4$, $n=2$) for pH=8.5-10.0, respectively.

On the other hand, the crystallization phenomena occurred at pH～4.5 and the crystallization reaction [24,25] was expressed as follows.

$$2[(NH_4)_3(H_3W_6O_{21})] + 18[NH_4OH] \rightarrow 12[(NH_4)_2(WO_4)] + 12[H_2O] \qquad (16)$$

$$12[(NH_4)_2(WO_4)] \rightarrow [(NH_4)_{10}(H_2W_{12}O_{42})\cdot 4H_2O] + 2[H_2O] + 14[NH_3] \qquad (17)$$

In the case of 4.5<pH condition, the white precipitates were observed in the IL phase. The obtained precipitates were removed by filtration and were dried at 298 K for 24 h. The XRD analysis of the obtained precipitates was shown in **Fig. 6** and the peak was in good agreement with the ammonium paratungstate (APT, $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 4H_2O$) described in JCPDS reference (No.01-076-6042). Then, APT is usually the final form required by the tungsten industry.
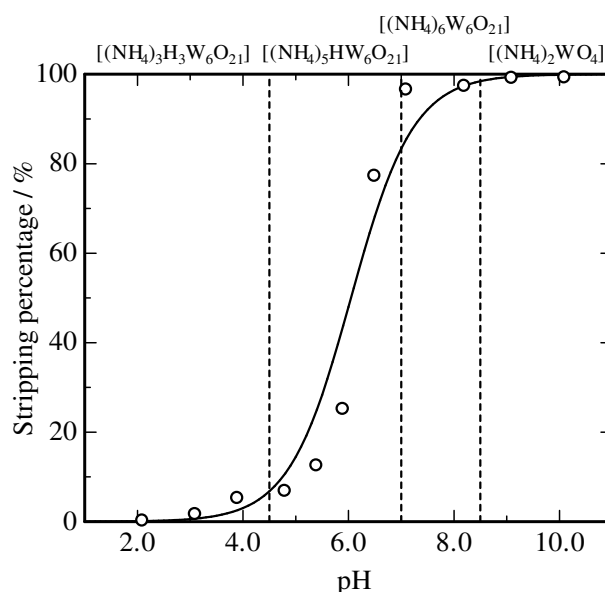
Fig. 5 Stripping behavior of W(VI) using 5% NH₄OH solution including NH₄Cl.
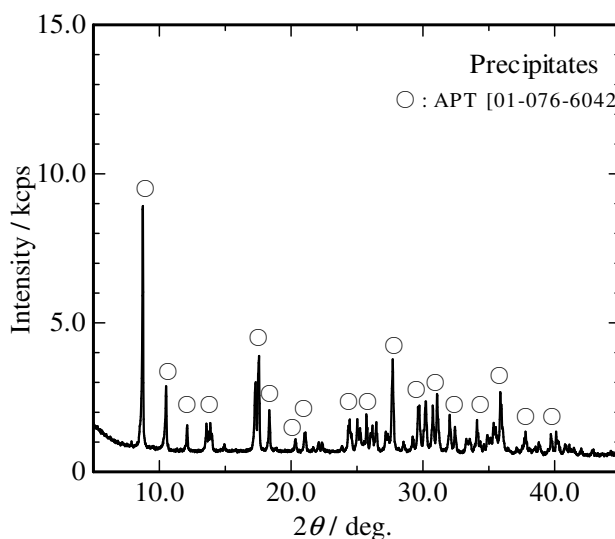
Fig. 6 XRD profile of the product obtained by crystallization-stripping process.

4. Conclusion

Solvent extraction (SX) process using $[P_{2225}][NTf_2]$ ILs with Alamine 336 extractant was applied to selectively separate W(VI) in the IL phase. From the plot of $\log D$ vs. $\log[A336]_{IL}$ at pH=1.0, the extraction mechanism of W(VI) using the $[R_3N]/[P_{2225}][NTf_2]$, $R=(CH_2)_7CH_3/(CH_2)_9CH_3$ system was based on the following reaction: $[H_3W_6O_{21}{}^{3-}]_{aq}$ + $3[R_3NH^+Cl^-]_{IL}$ $\rightleftarrows$ $[(R_3NH)_3H_3W_6O_{21}]_{IL}$ + $3[Cl^-]_{aq}$ Arrhenius plot could yielded the enthalpy (ΔH) and the entropy (ΔS). The positive ΔH value for W(VI) indicated the endothermic reaction. Then, ΔS value in pH=1.0 directly would be acted on the total negative alternation in Gibbs energy on the extraction reaction.

Moreover, the repeated use of $[R_3N]/[P_{2225}][NTf_2]$ medium was researched by continuous SX and stripping process. For the 5th cycles on SX, the extraction percentage of W(VI) at 91.6−98.4% was high value. The stripping efficiency using 3.0 mol dm^{-3} NH_4OH medium was also relatively high. The stripping percentage of W(VI) attained at 100 % at 8<pH by the following stripping reaction; $[(R_3NH)_n(H_xW_yO_z)]_{IL}$ + $n[NH_4OH]_{aq}$ $\rightleftarrows$ $[(NH_4)_n(H_xW_yO_z)]_{aq}$ + $n[R_3NH^+OH^-]_{IL}$. Furthermore, the crystallization reaction occurred at pH$\sim$4.5 and the white precipitates were obtained in the IL phase. The obtained precipitates were confirmed the ammonium paratungstate (APT, $(NH_4)_{10}(H_2W_{12}O_{42})\cdot4H_2O$) by XRD. Finally, a novel hydrometallurgical process was enabled us to demonstrate that it was effective to separate W(VI) from spent tungstophosphate catalyst.

References

[1] L. L. Murrell, D. C. Grenoble, C. J. Kim, N. C. Dispenziere, Supported transition metal oxides as acid cracking catalysts: Periodic trends and their relationship to activity and

selectivity, J. Catal., 107(2) (1987) 463-470. https://doi.org/10.1016/0021-9517(87)90310-1

[2] J. Bernholc, J. A. Horsley, L. L. Murrell, L. G. Sherman, S. Soled, Broensted acid sites in transition metal oxide catalysts: modeling of structure, acid strengths, and support effects, J. Phys. Chem., 91(6) (1987) 1526-1530. https://doi.org/10.1021/j100290a047

[3] G. C. Bailey, Olefin Disproportionation, Catal. ReV., 3(1) (1970) 37-60. https://doi.org/10.1080/01614947008076854

[4] Y. Wang, Q. Chen, W. Yang, Z. Xie, W. Xu, D. Huang, Effect of support nature on WO_3/SiO_2 structure and butene-1 metathesis, Appl. Catal. A: Gen., 250(1) (2003) 25-37. https://doi.org/10.1016/S0926-860X(03)00186-8

[5] F. Verpoort, A. R. Bossuyt, L. Verdonck, Olefin metathesis catalyst. Part II. Activation and characteristics of a 'molecular' tungsten unit on silica, J. Mol. Catal. A: Chem., 95(1) (1995) 75-82. https://doi.org/10.1016/1381-1169(94)00155-3

[6] J. P. Chen, R. T. Yang, Role of WO_3 in mixed V_2O_5-WO_3/TiO_2 catalysts for selective catalytic reduction of nitric oxide with ammonia, Appl. Catal. A: Gen., 80(1) (1992) 135-148. https://doi.org/10.1016/0926-860X(92)85113-P

[7] S. Djerad, L. Tifouti, M. Crocoll, W. Weisweiler, Effect of vanadia and tungsten loadings on the physical and chemical characteristics of V_2O_5-WO_3/TiO_2 catalysts, J. Mol. Catal. A: Chem., 208(1-2) (2004) 257-265. https://doi.org/10.1016/j.molcata.2003.07.016

[8] G. Baltin, H. Koser, K. P. Wendlandt, Sulfuric acid formation over ammonium sulfate loaded V_2O_5–WO_3/TiO_2 catalysts by $DeNO_x$ reaction with NO_x, Catal. Today, 75(1-4) (2002) 339-345.https://doi.org/10.1016/S0920-5861(02)00059-7

[9] M. Ai, Activities for the decomposition of formic acid and the acid-base properties of metal oxide catalysts, J. Catal., 50(2) (1977) 291-300. https://doi.org/10.1016/0021-9517(77)90038-0

[10] K. C. Kim, M. T. Pope, G. J. Gama, and M. H. Dickman, Slow Proton Exchange in Aqueous Solution. Consequences of Protonation and Hydration within the Central Cavity of Preyssler Anion Derivatives, $[|M(H_2O)|\supset P_5W_{30}O_{110}]^{n-}$, J. Am. Chem. Soc., 121(48) (1999) 11164-11170. https://doi.org/10.1021/ja992105b

[11] M. Misono, N. Mizuno, K. Katamura, K. Kasai, Y. Konishi, K. Sakata, T. Okuhara, and Y. Yoneda, Catalysis by Heteropoly Compounds. III. The Structure and Properties of 12-Heteropolyacids of Molybdenum and Tungsten ($H_3PMo_{12-x}W_xO_{40}$) and Their Salts Pertinent to Heterogeneous Catalysis, Bull. Chem. Soc. Jpn., 55 (1982) 400. https://doi.org/10.1246/bcsj.55.400

[12] I. V. Kozhevnikov, K.I. Matveev., Homogeneous catalysts based on heteropoly acids (review), Appl. Catal. A, 5(2) (1983) 135-150. https://doi.org/10.1016/0166-9834(83)80128-6

[13] M.T. Pope. Heteropoly and Isopoly Oxometalates. Inorganic Chemistry Concepts (8), Springer, New York, (1983).

[14] E. Lassner, From tungsten concentrates and scrap to highly pure ammonium paratungstate (APT), Int. J. Refract. Met. Hard Mater., 13(1-3) (1995) 35-44. https://doi.org/10.1016/0263-4368(95)00002-X

[15] B. D. Pandey, V. Kumar, D. Bagchi, R. K. Jana, Processing of tungsten pre-concentrate from low grade ore to recover metallic values, Miner. Process. Extr. Metall. Rev., 22(1) (2001) 101-120. https://doi.org/10.1080/08827509808962491

[16] T. Sato, K. Sato, Liquid-liquid extraction of tungsten (VI) from hydrochloric acid solutions by neutral organophosphorus compounds and high molecular weight amines, Hydrometallurgy, 37(3) (1995) 253-266. https://doi.org/10.1016/0304-386X(94)00066-C

[17] N.I. Gerhardt, A.A. Palant, V.A. Petrova, R.K. Tagirov, Solvent extraction of molybdenum(VI), tungsten (VI) and rhenium(VII) by diisododecylamine from leach liquors, Hydrometallurgy, 60(1) (2001) 1-5. https://doi.org/10.1016/S0304-386X(00)00123-7

[18] O. Glemser, W. Holznagel, W. Höltje, E. Sohwarzmann, Untersuchungen über Isopolywolframate, Z. Naturforsch. 20b (1965) 725-746.

[19] W.-H. Gu, Y. S. Jeong, K. Kim, J.-C. Kim, S.-H. Son, S. Kim, Thermal oxidation behavior of WC-Co hard metal machining tool tip scraps, J. Mater. Process. Technol., 212(6) (2012) 1250-1256. https://doi.org/10.1016/j.jmatprotec.2012.01.009

[20] P. Zhang, K. Inoue, K. Yoshizuka, H. Tsuyama, Extraction and selective stripping of molybdenum (VI) and vanadium (IV) from sulfuric acid solution containing aluminum(III), cobalt(II), nickel(II) and iron(III) by LIX 63 in Exxsol D80, Hydrometallurgy, 41(1) (1996) 43-53. https://doi.org/10.1016/0304-386X(95)00015-9

[21] D.R. Lide, CRC Handbook of Chemistry and Physics, New York (1993).

[22] Y. Song, Y. Tsuchida, M. Matsumiya, Y. Uchino, I. Yanagi, Separation of tungsten and cobalt from WC-Co hard metal wastes using ion exchange and solvent extraction with ionic liquid, Min. Engineer., 128 (2018) 224-229. https://doi.org/10.1016/j.mineng.2018.08.047

[23] K. Tsunashima, and M. Sugiya, Physical and electrochemical properties of low-viscosity phosphonium ionic liquids as potential electrolytes, Electrochem. Commun., 9(9) (2007) 2353-2358. https://doi.org/10.1016/j.elecom.2007.07.003

[24] E. Lassner, From tungsten concentrates and scrap to highly pure ammonium paratungstate (APT), Int. J. Refract. Met. Hard Mater., 13(1-3) (1995) 35-44. https://doi.org/10.1016/0263-4368(95)00002-X

[25] L. Luo, T. Miyazaki, A. Shibayama, W. Yen, T. Fujita, A novel process for recovery of tungsten and vanadium from a leach solution of tungsten alloy scrap, Min. Eng., 16(7) (2003) 665-670. https://doi.org/10.1016/S0892-6875(03)00103-1

[26] I. R.-M. Elizabeth, E. W. Israel, Structural Determination of Bulk and Surface Tungsten Oxides with UV−vis Diffuse Reflectance Spectroscopy and Raman Spectroscopy, J. Phys. Chem. C, 111(41) (2007) 15089-15099. https://doi.org/10.1021/jp074219c

[27] R.A.G. De Carvalho, M.N.M. Sampaio, Solvent extraction of tungsten by alkylamines-hydrochloric acid and alkylamines-sulphuric acid, Hydrometallurgy, 26(2) (1991) 137-150.

https://doi.org/10.1016/0304-386X(91)90027-J

[28] J. Coca, F. V. Diez, M. A. Moris, Solvent extraction of molybdenum and tungsten by Alamine 336 and DEHPA, Hydrometallurgy, 25(2) (1990) 125-135.

https://doi.org/10.1016/0304-386X(90)90034-Y

[29] T. K. Kim, R. W. Mooney, C. Chiola, Study of Soluble Tungstate Species by Solvent Extraction, Sep. Sci., 3(5) (1968) 467-478.

https://doi.org/10.1080/01496396808052230

[30] A. B. C. Sola, P. K. Parhi, J.-Y. Lee, H. N. Kang, R. K. Jyothi, Environmentally friendly approach to recover vanadium and tungsten from spent SCR catalyst leach liquors using Aliquat 336, RSC Adv., 10 (2020) 19736-19746. https://doi.org/10.1039/D0RA02229B